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SCIENTIFIC AND TECHNICAL ASSESSMENT REPORT ON MANGANESE

ENVIRONMENTAL PROTECTION AGENCY

APRIL 1975

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This report is a review and evaluation of the current knowledge of manganese in the environment as related to possible deleterious effects on human health and welfare. Sources, distribution, measurement, and control technology are also considered. Manganese is associated with small particles in the air. Concentrations measured in ambient air averaged 0.1 $\mu g/m^3$ (annual) with a maximum of 8.3 $\mu g/m^3$ (annual) near a large source.

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PREFACE

Although this report is issued in the Scientific and Technical Assessment Report Series, it differs in several respects from the comprehensive multi-media format that the Series will usually have because it was nearly completed prior to the creation of the STAR series in August 1974.

This document was prepared by a task force convened at the direction of Dr. John F. Finklea, Director, U.S. Environmental Protection Agency, National Environmental Research Center (NERC), Research Triangle Park (RTP), N.C. Assembly, integration, and production of the report were directed by the Special Studies Staff, NERC-RTP. The objective of the task force was to review and evaluate the current knowledge of manganese in the environment as related to possible deleterious effects upon human health and welfare. Information from the literature and other sources has been considered generally through May 1973.

A report prepared for the U.S. Environmental Protection Agency (EPA) by a National Academy of Sciences' Panel on Manganese of the Committee on Medical and Biological Effects of Environmental Pollutants served as a primary reference for this report.

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Review copies of this document also have been provided to other governmental agencies and to industrial and public interest groups.

All comments and criticisms have been reviewed and incorporated in the document where deemed appropriate.

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LIST OF ABBREVIATIONS AND SYMBOLS

AMP	Adenosine monophosphate
BaP	Benzo[a] pyrene
°C	Degrees Celsius
CO	Carbon monoxide
EDTA	Ethylenediaminetetraacetic acid
EPA	U. S. Environmental Protection Agency
g/gal	Grams per gallon
g/ha-mo	Grams per hectare per month
HC	Hydrocarbon
HCl	Hydrochloric acid
HNO_3	Nitric acid
H_2O	Water
H_2SO_4	Sulfuric acid
kg/km^2-mo	Kilograms per square kilometer per month
LD_{50}	Lethal dose to 50 percent of subjects
m/sec	Meters per second
m^3/day	Cubic meters per day
mg	Milligrams
mg/kg	Milligrams per kilogram
mg/liter	Milligrams per liter
mg/m^2-mo	Milligrams per square meter per month
mg/m^3	Milligrams per cubic meter
MMT	Methylcyclopentadienyl manganese tricarbonyl
Mn	Manganese
Mn^{2+},Mn^{3+},etc.	Manganese cations
$MnCl_2$	Manganese chloride
MnO_2	Manganese dioxide
MnO_3^{2-},MnO_4^{2-},etc.	Manganese anions
Mn_3O_4	Manganese oxide
MT	Metric tons
$\mu g/g$	Micrograms per gram
μg/liter	Micrograms per liter
μg/ml	Micrograms per milliliter
$\mu g/m^3$	Micrograms per cubic meter
μm	Micrometers (10^{-6} meters)
NAQCAC	National Air Quality Criteria Advisory Committee
NASN	National Air Surveillance Networks, EPA
NERC	National Environmental Research Center
ng	Nanograms
ng/cm^2	Nanograms per square centimeter
ng/m^3	Nanograms per cubic meter
NH_3	Ammonia
NO_x	Oxides of nitrogen
PHS	Public Health Service
ppb	Parts per billion
ppm	Parts per million
RTP	Research Triangle Park, N. C.
TEL	Tetraethyl lead

ABSTRACT

This report is a review and evaluation of the current knowledge of manganese in the environment as related to possible deleterious effects on human health and welfare. Sources, distribution, measurement, and control technology are also considered. Manganese is associated with small particles in the air. Concentrations measured in ambient air averaged 0.1 $\mu g/m^3$ (annual) with a maximum of 8.3 $\mu g/m^3$ (annual) near a large source.

In Norway, a form of pneumonia was attributed to airborne manganese in a community where concentrations were measured at 46 $\mu g/m^3$. Manganese poisoning characterized by progressive central nervous system deterioration has occurred under occupational exposure but apparently not from atmospheric exposure. Control of fine particulate emissions should reduce manganese emissions considerably.

SCIENTIFIC AND TECHNICAL ASSESSMENT REPORT ON MANGANESE

1. INTRODUCTION

The purpose of this document is to summarize the current knowledge of manganese in relation to its effects upon human health and welfare and the environment; and to evaluate this knowledge base with a view toward the need to control the release of manganese into the environment from anthropogenic (man-made) sources.

The U. S. Environmental Protection Agency (EPA) is required by the Clean Air Act as amended to promulgate standards and regulations for the control of air pollutants that are deleterious to human health and welfare. Human illness has been associated with excessive exposure to manganese. Decisions relating to the control of manganese as an air pollutant must be based not only upon knowledge regarding effects, but also on sources and subsequent ambient concentrations, transport and behavior in the environment, and available control technology. These aspects of the problem are reviewed to the extent deemed appropriate for decision-making processes. Sampling and analytical techniques are examined in order that the validity of available data may be evaluated.

It is generally accepted that manganese is an essential trace element for all living organisms; however, deleterious effects may result from excessive exposure. In this report, appraisals of effects are presented, and estimates of exposure-response relationships are noted when justified by available data. Manganese enters the human body principally via food, water, and air. The relative importance of each of these intake routes is examined. In addition, the principal anthropogenic sources of manganese are identified, and applicable control technology is assessed.

2. SUMMARY AND CONCLUSIONS

2.1 SUMMARY

Manganese (Mn) is among the trace elements least toxic to mammals; however, exposure to abnormally high concentrations resulting from anthropogenic sources has resulted in adverse human health effects. Manganese poisoning is characterized by progressive deterioration of the central nervous system, sometimes accompanied by unrelated pneumonitis.

The majority of cases have been associated with the breathing of manganese dust or fumes from mining or metallurgical operations. An outbreak of a form of pneumonia in inhabitants of Sauda, Norway, was attributed to manganese emissions from a ferromanganese plant. Absorption via the gastrointestinal tract and through the skin has also been reported. An outbreak of manganese poisoning in Japan was attributed to ingestion of manganese-contaminated well water. In the early stages of poisoning, removal of the victim from the polluted environment usually clears up manganism; however, in chronic cases, the effects on the central nervous system are not completely reversible.

Manganese has been classified as an essential trace element for both plants and animals, including man. Generally, organs and tissues do not accumulate large concentrations of manganese. Excretion normally occurs via the biliary route in the feces.

Plant species differ widely in manganese requirements and tolerances. The availability of manganese to plants is dependent upon the oxidation state of the manganese in soil. Excessive amounts of divalent manganese can be toxic to plants. Microbial action appears to play an important part in making manganese available to plants.

Manganese is one of the more abundant elements in the earth's crust. It is widely distributed in soils, sediments, rocks, and water; it is thought to be present in all organisms. At least 100 minerals contain manganese; however, it does not occur naturally as a metal. The concentration of manganese in soil ranges from near zero to 7,000 micrograms per gram (μg/g) with a rough average of about 850 μg/g. The concentration of dissolved manganese in sea water varies between 0.4 and 10 micrograms per liter (μg/liter) and in fresh water the concentration ranges from less than 1 to over 100 μg/liter. Manganese appears to be omnipresent in foodstuffs, with concentrations ranging from a trace to 275 μg/g. The maximum concentrations of manganese in foodstuffs are found in nuts, tea, and spices.

The 1970 total consumption of manganese in the United States was over a million metric tons. Most of the concentrate is used in the production of ferromanganese. Approximately 90 percent of the manganese consumed in the United States goes into production of iron and steel where it nullifies the effects of sulfur, no substitute material has been found for this purpose. Manganese is also used as an alloying agent for steel, aluminum, and copper. Other uses include the manufacture of dry cell batteries, welding rod coatings and fluxes, dyes, paints, varnish dryers, fungicides, and pharmaceuticals. Manganese compounds are added to boiler and turbine fuels to improve combustion and suppress smoke and are used as antiknock agents in gasoline.

The principal sources of ambient environmental pollution by manganese are emissions from metallurgical processing plants and reprocessing waste materials. Emissions to the atmosphere from industrial plants and processes will vary considerably, depending upon the process involved and the degree of control exercised.

Particle emissions from a ferromanganese blast furnace are generally in two size ranges; dust particles >20 micrometers (μm), and fume with particle sizes ranging from 0.1 to 1.0 μm. It has been reported that the dust particles comprise approximately 20 percent of the total particulate emissions, and fumes approximately 80 percent.

The reported mass median diameter of suspended particles containing manganese in the ambient air is approximately 2.0 μm.

With the use of available control technology, the unit contribution to the ambient atmospheric concentration of manganese should be relatively small from iron and steel. It has been estimated that over 80 percent of the total national manganese emissions in 1968 was from iron, steel, and ferroalloy production. Dust from the handling of raw materials in metallurgical processing, and other production activities such as the manufacture of chemicals, fertilizers, fungicides, and dry cell batteries, may result in local manganese pollution problems.

Disposal of waste products may contribute to the manganese contamination of local water sources. Few cases of manganese contamination of soil have been reported. Such contamination would come primarily from fertilizers, fly ash, and mine effluents.

Manganese has been found in measurable amounts in practically all samples of suspended particulate matter collected by the National Air Surveillance Networks (NASN) from the air of some 300 urban areas. The highest concentrations, as expected, are found in the vicinity of ferromanganese alloy plants or related activities. The NASN urban average manganese concentration is less than 0.2 microgram per cubic meter ($\mu g/m^3$), but several cities have annual averages in the 0.5 to 3.3 $\mu g/m^3$ range. Occasional 24-hour concentrations as high as 14.0 $\mu g/m^3$ have been measured. Annual averages as high as 8.3 $\mu g/m^3$ have occurred in small communities located near a large point source in the highly industrialized Kanawha River Valley of West Virginia. In Norway, concentrations of over 46 $\mu g/m^3$ have been reported in the vicinity of a ferromanganese furnace. Approximately 80 percent of manganese in the suspended particulate matter from six large cities in the United States was associated with particles in the respirable size range—that is, 5 μm or less in diameter. The existence of manganese in the smaller particles favors a widespread distribution of this pollutant. Such distribution has been confirmed by the analysis of precipitation samples collected at many remote locations in the United States.

Manganese in the atmosphere is associated primarily with particulate matter. Thus, the principal mechanisms for manganese removal from the air are precipitation, gravitational settling, and absorption at the earth's surface. Manganese may be involved in the atmospheric conversion of sulfur dioxide to sulfuric acid, although in the presence of ammonia, the manganese concentrations in the ambient air may not be high enough to affect that conversion. The reaction, however, of manganese dioxide with nitrogen dioxide to form manganese nitrate may occur in the atmosphere.

The use of presently available control technology for stationary sources would reduce manganese emissions to the atmosphere. Availability of control technology for fine particulates would further reduce emissions to the atmosphere.

2.2 CONCLUSIONS

The natural abundance of manganese, and its dynamic behavior in the environment—which involves physical, chemical, and biological activity—make it difficult to assess the contribution and effects of man-made sources. Much of our knowledge concerning the toxicity of manganese is based upon clinical studies of individuals with manganese poisoning resulting from exposure to high concentrations. Much remains unknown about the biochemical and toxicological effects of manganese. No cases of manganese poisoning have been reported from exposure to concentrations less than the recommended occupational threshold limit of 5 mg/m^3 (8 hours per day, 40 hours per week), although some argue that the safety

margin is low for susceptible persons. Based upon the present state of knowledge and available data, the following conclusions can be drawn:

- Manganese is an essential element for all living things.
- Adverse health effects may occur from exposure to high concentrations of manganese, particularly in the form of dust and fumes.
- There is currently no evidence that human exposure to manganese at the levels commonly observed in the ambient atmosphere results in adverse health effects. The only human health effects attributable to manganese in ambient air were found in persons living in the immediate vicinity of two major point sources in Norway and Italy. Manganese pollution is presently a local problem, but the widespread use of manganese fuel additives would make man-made emissions more ubiquitous. There is no evidence that predicted manganese concentrations resulting from the use of methylcyclopentadienyl manganese tricarbonyl would result in adverse health effects; however, respiratory irritant effects from long-term or frequent exposure to low concentrations have not been thoroughly investigated.
- Most effects from manganese in humans appear to result from prolonged inhalation.
- Manganese pollution of water does not appear to be a problem except possibly in isolated cases of waste disposal.
- Atmospheric concentrations of manganese observed in urban areas can be attributed primarily to man-made sources. The principal source of atmospheric emissions is metallurgical processing.
- Particulate control technology available and/or under development should be adequate to maintain the atmospheric concentration of manganese at an acceptable level; however, control of fine particulate matter that contains manganese remains to be evaluated as this technology is applied.

3. CHEMICAL AND PHYSICAL PROPERTIES

Manganese (Mn) does not occur naturally as a metal; however, over 100 minerals contain manganese as a natural constituent. Among manganese-containing minerals are sulfides, anhydrous and hydrous oxides, carbonates, anhydrous and hydrous silicates, anhydrous and hydrous phosphates, arsenates, tungstates, and borates. Oxides, carbonates, and silicates are the most important. Like iron, manganese occurs in the divalent and trivalent forms. The chlorides, nitrates, and sulfates of manganese are highly soluble in water, but the oxides, carbonates, and hydroxides are only sparingly soluble. Two reviews provided the following information.[1,2]

Manganese is a gray-white metal resembling iron, but it is harder and more brittle. It is especially noted for imparting hardness to metal alloys. The physical and chemical properties of manganese and some of its compounds are listed in Table 3.1.

Table 3.1. PROPERTIES OF MANGANESE AND SOME OF ITS COMPOUNDS[1,2]

Name	Chemical symbol or formula	Atomic or molecular weight	Specific gravity	Melting point, °C	Boiling point, °C	Solubility
Manganese	Mn	54.94	7.2	1244±3	1962	Reacts in hot or cold H_2O. Soluble in dilute acid.
Manganese dioxide	MnO_2	86.94	5.026	(–0)535		Insoluble in hot or cold H_2O, HNO_3, or acetone. Soluble in HCl.
Manganous carbonate	$MnCO_3$	114.94	3.125	Decomposes		65 mg/liter (25°C) Soluble in dilute acid. Insoluble in NH_3 and alcohol.
Manganous chloride	$MnCl_2$	125.84	2.997 (25°)	650	1190	622 g/liter (10°C) 1238 g/liter (100°C) Soluble in alcohol. Insoluble in ether and NH_3.
Manganous acetate	$Mn(C_2H_3O_2)_2 \cdot 4H_2O$	245.08	1.589			Soluble in cold H_2O and alcohol.
Potassium permanganate	$KMnO_4$	158.04	2.703	Decomposes	<240	28.3 g/liter (0°C) 250 g/liter (65°C) Decomposes in alcohol. Soluble in H_2SO_4. Very soluble in methyl alcohol and acetone.

Manganese can exist in eight different oxidation states (0, 1+, 2+, 3+, 4+, 5+, 6+, 7+), of which the bivalent form (Mn^{2+}) is the most stable. Elemental manganese is a highly reactive metal. The lower oxidation states are usually in the form of cations (e.g., Mn^{2+}, Mn^{3+}, Mn^{4+}), while the higher oxidation states form anions (e.g., MnO_3^{2-}, MnO_4^{1-}).

The toxicity of manganese compounds appears to depend upon the type of manganese ion present and the oxidation state of manganese. It has been suggested that manganese cations are more toxic than the anion forms. The permanganate anions, although strong oxidizing agents which show some caustic action, are relatively less toxic than the cations. The bivalent cation is said to be 2.5 to 3 times more toxic than the trivalent cation. While manganese oxides such as MnO, Mn_3O_4, Mn_2O_3, and MnO_2 are toxic to rats, the higher oxides appear to be the most toxic. The associated anion is reported to affect the toxicity of manganese; for example, manganese citrate is more lethal than manganese chloride.

Mn has three principal uses: In steelmaking as a reagent to reduce oxygen and sulfur and as an ingredient in special alloy steels; in the manufacture of dry-cell batteries for depolarization; as MnO_2, and in the chemical industry, as an oxidizing agent, for the production of potassium permanganate and other manganese chemicals. Manganin, an alloy containing manganese, copper, and nickel, is used in electric resistance coils. Manganese also is one of the components of manganese-bronze and certain alloys with desirable magnetic properties. Several salts are used as driers for linseed oil. The manganates and permanganates are oxidizing agents used for disinfection, bleaching, and as laboratory reagents. Manganous acetate is used in dyeing, tanning of leather, in fertilizers, and as a chemical catalyst. Manganese sulfate is used as a trace element in poultry and animal feeds. Organic manganese compounds are added to vehicular and stationary source fuels as smoke inhibitors and to vehicular fuels as antiknock agents.

Manganese and its compounds are active chemicals which either react with materials or catalyze other reactions. Their effect on catalytic oxidation appears to be of prime importance in relation to air pollution. Sulfur dioxide and nitrogen dioxide react readily with manganese dioxide to produce soluble sulfates, dithionates, and nitrates. These reactions have been utilized to remove sulfur dioxide from flue gases; more important is the fact that small amounts of manganese, usually as manganese sulfate formed in the reaction of manganese dioxide with sulfur dioxide, will catalyze the oxidation of sulfur dioxide to sulfur trioxide.

Most manganese emissions to the atmosphere are in the form of oxides. However, in the presence of sulfur dioxide and nitrogen dioxide, these oxides are rapidly converted to sulfates and nitrates.

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4. MEASUREMENT TECHNIQUES

4.1 SAMPLING

4.1.1 Ambient Air

Analytical procedures presently available require collection on filters of the particulate matter containing manganese. The filter material must be chosen with great care so that trace amounts of manganese in the filter do not distort the results. A typical glass-fiber filter contains about 400 nanograms per square centimeter (ng/cm^2) of manganese,[1] which would correspond to a concentration of 70 nanograms per cubic meter (ng/m^3) if the filters were used in a high volume sampler operating for 24 hours at a flow rate of 1.5 cubic meters per minute. Specially selected flash-fired glass-fiber filters with only 20 ng/cm^2 of manganese were found acceptable for use by the National Air Surveillance Networks (NASN).[3] Organic membrane filters contain 10 ng/cm^2 of manganese.[3] In view of the measured size distributions for particles in ambient air,[4] the filtration efficiency for 0.3 micrometer (μm) particles should be at least 99 percent. The efficiencies of various filter media have been studied by Lockhart et al.[5]

4.1.2 Water

The following considerations are important in sampling water for manganese: selection of sampling sites, frequency of sampling, sampling equipment, and sample preparation. Brown et al.[6] provide more specific information.

Particulate matter may be filtered from water by use of membranes or other suitable filtration material. Once the particulates are collected on a filter, the analytical problems are almost identical to those described for analysis of air. The methods of optical spectroscopy, neutron activation, and X-ray fluorescence are all useful and have some of the same advantages and limitations that they have for the analysis of particulates in air. Atomic absorption is the standard EPA method for determining manganese in water.[7]

4.1.3 Food

There are no particular difficulties in obtaining food samples. After collection of the samples, handling depends on the methods of analysis. Except for analysis by neutron activation, the samples are ashed by wet or dry methods, and the manganese is acid-extracted. For instrumental neutron activation analysis, the sample is analyzed without prior preparation.

4.1.4 Soil

The aim of soil sampling is to obtain a sample representative of a particular area. Problems arise in areas having soils of variable composition where large sampling errors can occur. The sampling error can be estimated by obtaining duplicate samples from random sites within a sample area. A given sample can be analyzed twice to determine the precision of the laboratory method.[8]

4.1.5 Biological Tissues

The manganese content of body fluids or tissues is not a reliable index of exposure to manganese. Blood or urine from persons with signs or symptoms of manganese poisoning have not shown high levels of manganese. There is, however, a rough correlation between urine levels and average air concentrations.[9] The average concentration of manganese is 1 to 8 micrograms per liter (μg/liter) for urine and 2 to 10 micrograms per 100 grams for blood.[9]

Some evidence indicates that manganese concentrates in hair after exposure to increased concentrations. The use of hair as an indicator of exposure is complicated by the fact that manganese in hair is associated with the structures which confer hair color. Very low concentrations are associated with white hair and other unpigmented structures.

4.1.6 Stationary Source Emissions

Two factors are essential to obtaining reliable emission data–a sampling procedure that provides representative samples and an analytical method that has the required sensitivity, selectivity, and accuracy.

Sampling of stationary air pollution sources for manganese must be done isokinetically by means of a sampling train with substantial efficiency for removing manganese. The source sampling train,[10] EPA Method 5, is shown in Figure 4.1. Particulates collected in the probe, on the filter, and in the water-filled impingers are analyzed for manganese.

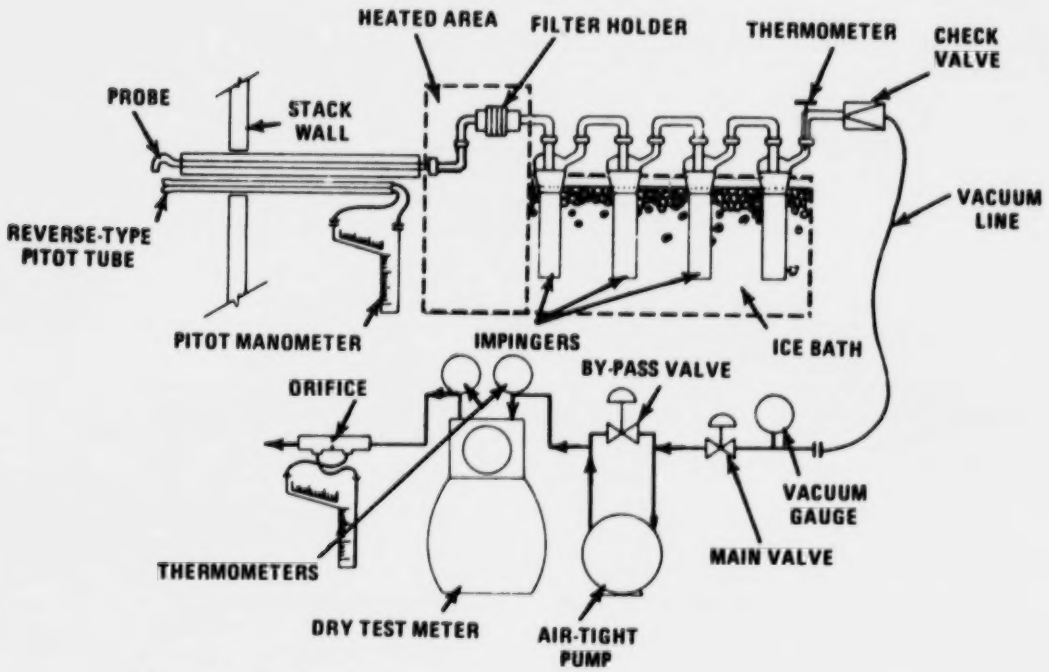

Figure 4.1. Particulate sampling train used for collecting manganese.[10]

4.1.7 Mobile Source Emissions

Manganese is emitted from mobile sources as a component of particulate matter. Concentrations in emissions from these sources vary, depending upon the trace manganese levels in the fuel or fuel additives, if any. Mobile source particulates may be collected by total or proportional sampling of the hot exhaust or by proportional sampling of the exhaust mixed with dilution air; the latter allows cooling and condensation of the higher-molecular- weight organics associated with short-time ambient exhaust particulates. The latter method also provides a more realistic assessment of the mass and composition of the primary mobile-source particulate. Collection with this technique can be by means of a single filter, multiple filter, beta gauge, or particle size fractionating device. The particulate can then be analyzed directly or after dissolution in an appropriate solvent. Gaseous samples may be collected by the cold trap technique or on a chromatographic column.

4.2 ANALYTICAL TECHNIQUES

4.2.1 Inorganic Manganese Compounds In Air

4.2.1.1 Optical Spectroscopy–Spectrographic methods have been used extensively to detect and quantify manganese and other trace metals in air samples and other materials. With suitable variations in sample preparation, available standard methods can be used equally well for air or for biological samples having manganese concentrations in the microgram range. Cholak and Hubbard[11] describe a spectrochemical method in which the manganese is isolated from interferences and concentrated in a small volume by complexing with sodium diethyl-dithiocarbamate and extracting with chloroform before analyzing with the spectrograph. Tabor and Warren[12] briefly discuss a semiquantitative method suitable for estimation of trace metals, including manganese, in samples collected on glass-fiber filters such as those commonly used in sampling community air. Spectroscopy has several advantages: it can be made specific, or nearly so, for almost any element; it has adequate sensitivity for most types of air samples; and it can be used to determine a number of elements in the sample concurrently. A disadvantage is that a substantial investment in space and money is necessary. Also, a high degree of skill is needed in this rather specialized field of analysis.

In the field procedure used by the NASN, atmospheric particulate matter is collected on a glass-fiber filter that is returned to the laboratory.[3] A portion of the filter is ashed in a 1-Torr oxygen atmosphere for 1 hour at 150°C. The trace elements are extracted by refluxing for 3 hours with an acid mixture.[13] Presumably this extraction procedure removes trace elements from the particulate with a much higher efficiency than it does the elements in the filter blank. The recovery of particulate manganese by this procedure has been determined to be quite good. By means of a high resolution grating emission spectrometer, NASN personnel routinely analyze for manganese as well as for 15 other elements. The sensitivity for manganese is 10 ng/m^3, assuming a 2200-cubic meter (m^3) air sample.[3]

4.2.1.2 Atomic Absorption–The use of atomic absorption analysis for trace metals, including manganese, in the atmosphere was described recently.[1,13] This method has advantages over other methods. It is relatively simple to use and is highly specific for a given element. Its sensitivity is at least as good as, and in many cases is better than, that of other methods. Using the same extraction procedure as that used for emission spectroscopic analysis, Thompson et al.[13] found a sensitivity of 1 nanogram per cubic meter (ng/m^3), assuming a 2000-m^3 air sample. The method is fairly free of interferences, except for possible matrix effects, which can generally be avoided by diluting the sample solution so that the content of dissolved solids is less than 0.5 percent. When glass-fiber filters are used, silica extracted from the fibers can interfere with the determination of manganese, zinc, iron, and possibly other elements, unless they are removed by the presence or addition of calcium to the solution[14] before the sample is subjected to atomic absorption analysis. This method has also been used to determine manganese in water and in other materials. The sensitivity varies from 1 to 5 μg/liter depending on the material being analyzed.[13] Flameless atomic absorption spectroscopy, a modification of the basic technique, is sensitive to 0.02 μg/liter of

manganese in solution.[2] In view of these concentrations and the fact that little or no sample preparation is required, atomic absorption spectroscopy is well suited to the analysis of manganese in solution.

4.2.1.3 Neutron Activation–Neutron activation analysis has been found most suitable for the determination of very low concentrations (nanogram range) of manganese, as well as up to 32 other elements. With this method, it is essential that the particulate matter be collected on filters that are very low in trace elements. Certain membrane and ashless paper filters have been found to be quite satisfactory. With the use of a polystyrene filter, a sensitivity of 0.6 ng/m^3 has been reported by Dalton et al.[15] An advantage of the neutron activation method is that it is nondestructive. The manganese reaction product has a relatively short half-life (2.58 hours), but one that is long enough so that the manganese content can be determined after a brief cooling period following exposure to the neutron flux.

Manganese was one of 15 chemical elements analyzed in an interlaboratory study. Compared with the certified concentration value determined by the National Bureau of Standards, participating laboratories achieved substantial accuracy with instrumental neutron activation analysis of coal and fly ash. Table 4.1 summarizes the accuracy of various analytical methods used in this study.[16] Neutron-activation analysis is generally more sensitive than other analytical methods. By way of comparison, the sensitivity for manganese by several analytical methods is shown in Table 4.2.[15]

Table 4.1. ACCURACY OF METHODS FOR ANALYSIS OF MANGANESE IN COAL AND FLY ASH[16]

Analytical method	No. labs compared		Accuracy, %[a]	
	Coal	Fly ash	Coal	Fly ash
Instrumental neutron activation analysis	7	8	5.3	5.5
Atomic absorption spectrophotometry	14	14	14.8	13.6
Optical emission spectroscopy	3	3	12.6	4.6

[a]The signed difference between the mean value of measured analysis and the accepted true value expressed as a percent of the accepted true value:

$$\text{accuracy, \%} = \frac{X_{True} - X}{X_{True}} \times 100$$

Table 4.2. SENSITIVITY OF ANALYTICAL METHODS FOR MANGANESE

Analytical method	Detection limit, nanograms
Neutron activation analysis	0.005
Optical emission spectroscopy (DC arc)	10.
Atomic absorption spectrophotometry	0.5
Spark source mass spectrometry	0.05

4.2.1.4 Spark Source Mass Spectrometry—Manganese in gasoline can be analyzed satisfactorily by the use of spark source mass spectrometry. The preparation procedure involves an oxidation step with bromine after the addition of an erbium spike. This is followed by freeze-drying to remove the liquid and a final drying at 17°C to remove the odors of gasoline. The residue remaining is mixed with graphite until homogenous, and an electrode is pressed for analysis; the spark source mass spectrometer is equipped with photographic plate output.[17]

4.2.1.5 X-ray Fluorescence—Where speed and the cost of analysis are not of major concern, the methods discussed above are more than adequate. The use of an X-ray fluorescence spectrometer, however, offers the opportunity for a low-cost nondestructive elemental analysis in less than 10 minutes. Birks et al.[18] analyzed a number of particulate samples from stationary sources, using a conventional crystal diffraction spectrometer. With an analysis time of 100 seconds per element, they reported the concentration of 12 elements. The sensitivity for manganese on a Whatman 41 filter is estimated to be 30 ng/cm^2. For a 24-hour sampling period, at a flow rate of 7 liters per minute per square centimeter this corresponds to a sensitivity of 3 ng/m^3. Birks[18] made a complete elemental analysis with much greater sensitivity in 100 seconds, using multichannel analyzers with 14 to 24 crystals.

Advances in electronics and in solid state detectors for X-rays by Goulding et al.[19-21] created widespread interest in energy dispersive X-ray fluorescence spectroscopy. Using this technique, Giaque et al.[22] analyzed a number of types of specimens including air filters for at least 12 elements, and Rhodes et al.[23] conducted an extensive elemental analysis—for up to 15 elements – of the suspended particulate matter collected at 38 stations in Texas. Various methods of excitation of samples for X-ray analysis were studied by Cooper.[24] His study indicates that use of either X-ray tubes or radioactive sources is the most efficient and cost-effective for routine analysis.

Goulding[25] developed a prototype automated sampling station and X-ray analysis system. The analytical system uses an X-ray tube with three separate secondary fluorescers. A detection limit of 5 ng/m^3 for manganese is obtained for a 300-second analysis by the use of a copper fluorescer, along with a 0.8-μm pore-size millipore filter that has been sampling air for 2 hours. In the presence of excessively high concentrations of iron in the atmosphere, the method will be less sensitive for manganese. X-ray fluorescence may be used to analyze manganese in solutions if the sample is prepared by freeze drying.

4.2.1.6 Wet Chemical Methods[9]—The periodate method is the classic wet chemical method of analyzing air samples for manganese. It can be used in almost any chemical laboratory with relatively simple equipment. The final colorimetric estimation of permanganate formed by oxidation of manganese can be made satisfactorily with Nessler tubes, if necessary. The sensitivity is rather poor, however, in comparison with that of other methods.

The technique has also been widely used for determining total manganese in the soil, for which it is rapid and reliable. The intensity of the permanganate color is stable and reproducible if no reducing agents are present. This method is considered to give a poor estimate of manganese available to plants. The colorimetric method[26] has been widely used, however, for analysis of soils.

Because manganese may exist in water-soluble form, as exchangeable Mn^{2+}, as organically bound manganese, and as various oxides of manganese, analytical techniques have been developed to determine the amounts of manganese present in each of these forms. Because of the importance of manganese in plant nutrition, emphasis has been placed on developing methods to determine its availability to plants.

The availability of manganese to plants has usually been measured as divalent manganese in soil solution and as exchangeable manganese. The former is extracted with water, and the latter is measured by extracting soil with a strong salt solution: a 1 molar solution of calcium or magnesium nitrate is widely used.

Insoluble oxides of divalent and tetravalent manganese are reduced to the soluble divalent form. Measurements of the amounts of trivalent and tetravalent forms give an indication of the relative research power of the soil for producing soluble manganese.

4.2.2 Organic Manganese Compounds in Air

Although it is unlikely that manganese would be present in organic form in the ambient air, it is desirable to develop a method for sampling and analyzing air for these compounds to confirm their presence or absence. No such method appears at hand in the scientific literature. It seems logical that some of the procedures presently being used for the determination of methylcyclopentadienyl manganese carbonyl in gasoline or other liquid fuels might be modified to determine these compounds in the atmosphere. A number of methods developed for other metal carbonyls could be modified to determine manganese carbonyls. A recent Russian publication cited in the National Academy of Sciences report[9] mentions a method for determining cyclopentadienyl manganese tricarbonyl vapor in air, developed by M. S. Bykhovskays, but gives no reference to pertinent literature or to procedural details.

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5. ENVIRONMENTAL APPRAISAL

5.1 ORIGIN AND ABUNDANCE

5.1.1 Natural Sources

Manganese ore deposits are widespread throughout the tropical and warmer temperature zones of the earth. The largest deposits are in the Caucasus and the Dnieper Basin of Russia and in Mainland China. In the United States, lower grade ores are found in the Appalachian and Piedmont regions, in Arkansas, and in the western states. Surrounding areas can be assumed to have an abnormally high concentration of manganese in soil and water.

Manganese is considered to be the 12th most abundant element in the earth's crust. It is exceeded in abundance, for example, by aluminum, iron, magnesium, and titanium, but is more abundant than nickel, copper, uranium, zinc, lead, and vanadium. The concentration of manganese in the earth's crust ranges from near zero to 7,000 $\mu g/g$. The highest concentrations are found in clay and deep-sea sediment. Pyrolusite, a mineral form of manganese dioxide, is one of the more common manganese oxide minerals. An abundance of manganese nodules has been found on the deep ocean floor. Insofar as is known, all plants and animals contain manganese.

5.1.2 Man-Made Sources

5.1.2.1 Stationary Sources – Approximately 90 percent of the manganese produced is used in metallurgical processes, primarily in the form of ferromanganese. Either synthetic or natural dioxide is used in the manufacture of batteries, and a variety of manganese or manganese-containing ores are used in the chemical industry. The primary uses of manganese are summarized in Tables 5.1 and 5.2.[1]

Table 5.1. CONSUMPTION OF MANGANESE ORE IN THE UNITED STATES, 1970[1]

Use	Gross weight of ore,[a] metric tons
Manganese alloys and metal	1,889,483
Pig iron and steel	96,960
Dry cells, chemicals, and miscellaneous	141,100
Total	2,127,543

[a]By definition, manganese ore contains at least 35 percent manganese (natural).

Table 5.2. CONSUMPTION OF MANGANESE ALLOYS AND METAL IN THE UNITED STATES, 1970, BY END USE[1]

Use	Gross weight, metric tons				
	Ferromanganese		Silico-manganese	Spiegeleisen	Manganese metal[a]
	High-carbon	Medium- and low-carbon			
Steels:					
Carbon	642,313	82,395	79,061	10,052	4,353
Stainless and heat-resisting	1,647	4,438	7,534	--[b]	6,020
Alloy (excluding stainless and tool)	97,239	24,785	24,167	1,511	1,764
Tool	755	110	--[b]	--	--[b]
Cast irons	7,624	2,109	6,439	6,578	10
Superalloys	393	40	--	--	327
Alloys (excluding alloy steels and superalloys)	4,848	1,055	1,654	--	8,469
Miscellaneous and unspecified	29,181	1,619	5,796	100	1,091
Totals	784,000	116,551	124,651	18,241	22,034

[a]Nearly all electrolytic.

[b]Withheld to avoid disclosing individual company confidential data; but included in "Miscellaneous and unspecified."

Manganese is emitted from various sources primarily as manganese oxides. Because of its many valence states, however, manganese may interact with other substances to form many compounds.[2] Physical forms emitted are particulate in nature, and more than 50 percent of these particulates are in the submicron particle size range.[2]

In 1968 about 17,000 metric tons (MT) of manganese were emitted into the atmosphere over the United States (Table 5.3). About 47 percent resulted from production of ferroalloys and about 37 percent from the production of iron and steel.[3] Coal was also a significant source of manganese emissions.

Manganese concentrations in emissions depend on several factors, including manganese content of raw material and/or fuel, process type, method of operation, and the efficiency of the particulate control system. Therefore, a source emission concentration range rather than a specific emission factor is reported for selected stationary sources. Table 5.4 summarizes the manganese concentration range in particulate emissions collected isokinetically downstream from control systems for several source categories.[4,5]

Table 5.3. ESTIMATED MANGANESE EMISSIONS BY SOURCE, 1968[2]

Source category and group	Emissions, metric tons
Mining	5
Processing	
Manganese metal	290
Manganese alloys	8,050
Total	8,340
Reprocessing	
Carbon steel	3,910
Cast iron	2,490
Welding rods	20
Nonferrous alloy	50
Batteries	80
Chemicals	270
Total	6,820
Consumptive uses	
Coal	1,760
Oil	6
Total	1,766
Incineration and other disposal	
Sewage and sludge	160
All sources	17,091

Table 5.4. RANGE OF MANGANESE CONCENTRATIONS IN SOURCE EMISSION PARTICULATES[4]

Source	Concentration, μg/g[a]
Coal-fired power plants	1 to 1,000
Lead smelters	0.01 to 1
Cement plants	100 to 1,000
Iron and steel foundries	10 to 1,000
Municipal incinerators	100 to 1,000

[a]Samples collected with EPA Method 5 sampling train[5] and analyzed by optical emission spectroscopy.

Recently, coal-fired power plants have been the subject of several material balance studies for trace metals. An in-depth study was done on the Allen Steam Plant at Memphis, Tennessee (Table 5.5). This power plant is a 240-megawatt unit operated at 80 percent of full load. Based on the results from the electrostatic precipitator inlet and outlet, the efficiency for manganese removal is higher than 90 percent.[6]

Considerable research is under way to determine trace element concentration by particle size. A study of sized fly ash from three coal-fired power plants found the manganese concentration evenly distributed by particle size (Table 5.6).[7]

Table 5.5. MATERIAL BALANCE FOR MANGANESE AT A COAL-FIRED STEAM POWER PLANT[6]

Run No.	Mass flow, g/min[a]				Precipitator efficiency, %
	Coal	Slag tank solids	Fly ash		
			Precipitator inlet	Precipitator outlet	
5	66	41	22	---	---
7	64	39	21	0.62	97
9	67	46	16	1.1	93

[a]Samples collected isokinetically using an alundum filter followed by a millipore filter and analyzed by instrumental neutron activation.

Table 5.6. MANGANESE CONCENTRATION IN COAL FLY ASH, BY PARTICLE SIZE[7,a]

Particle size, μm	Concentration, μg/g		
	Source A	Source B	Source C
1.3	270	328	256
2.0	189	334	235
4.6	157	339	317
8.5	122	344	255
13.0	156	344	208
22.0	148	363	221
33.0	156	370	219
>33.0	158	301	246

[a]Fly ash sized using a Bahco classifier and analyzed by instrumental neutron activation.

Roughly 90 percent or more of the manganese consumed in the United States is used in the production of iron and steel.[8] A source emission inventory in a highly industrial area with uncontrolled iron and steel manufacturing should reflect the high emissions from this source. Calculated emissions for the large industrial area of Chicago, Milwaukee, and Northwest Indiana, where iron and steel manufacturing is the predominant source of manganese emissions, do indeed reflect high emissions (Table 5.7).[9]

Table 5.7. MANGANESE EMISSIONS FROM AIR POLLUTION SOURCES IN THE CHICAGO, MILWAUKEE, AND NORTHWEST INDIANA AREA[9]

Source	Emissions, metric tons/year
Coal burning	60
Coke burning	5
Fuel oil burning	5
Iron and steel manufacturing	4,500

5.1.2.2 Fuels–Manganese concentrations for coals mined in various areas of the United States are summarized in Table 5.8.[10,11] Table 5.8 also summarizes the manganese contents of selected residual fuel oils and crude oils.[12] One type of fuel oil, residual fuel oil No. 6, is commonly used in electric power plants and large industrial boilers. Crude oil is of concern because several power plants have shifted from burning residual fuel oil to burning crude oil directly due to the increasing cost of low-sulfur residual fuel oil.[13] As of February 1972, three East Coast utilities were burning a total of 5,400 m^3/day of crude oil, an amount which has greatly increased in the last few years.

As part of EPA's Nationwide Fuel Surveillance Network, gasoline is collected by the 10 EPA Regions for extensive analysis. Samples are analyzed for approximately 25 elements, including manganese. Table 5.8 includes a summary of manganese concentrations in gasolines collected in the spring of 1972. The gasolines collected were from retail service station pumps and represent fuels used in motor vehicles at the time and in the area of collection.[14]

5.1.2.3 Consumer-Purchased Fuel Additives and Motor Oil–In anticipation of regulations on the registration of fuels and fuel additives, pursuant to Section 211 of the 1970 Clean Air Act, EPA has started to analyze consumer-purchased fuel additives for trace elements. As the first step of this surveillance effort, fuel additives were purchased from retail stores in the Research Triangle Park area and analyzed for trace elements. The manganese content of these off-the-shelf additives are shown in Table 5.8.[15]

As part of the EPA's Nationwide Fuel Surveillance Network, crankcase lubricating oils are being collected for trace element analysis. Table 5.8 shows the manganese content of several grades of one brand of motor oil.[16]

Table 5.8. MANGANESE CONCENTRATIONS OF COAL, FUEL OIL, CRUDE OIL, GASOLINE, FUEL ADDITIVES, AND MOTOR OIL[10,16]

Sample	Number of samples	Average concentration	Range
Coal	76	37 μg/g	5 to 80 μg/g
Residual fuel oil	20	0.136 μg/g	0.012 to 0.27 μg/g
Crude oil	20	0.031 μg/g	<0.001 to 0.15 μg/g
Regular gasoline			
Brand A	10	0.005 μg/ml	<0.001 to 0.01 μg/ml
Brand B	9	0.0066 μg/ml	<0.001 to 0.01 μg/ml
Premium gasoline			
Brand A	10	0.0144 μg/ml	0.002 to 0.03 μg/ml
Brand B	8	0.0052 μg/ml	0.002 to 0.02 μg/ml
Fuel additives			
Gas treatment	3	0.038 μg/ml	0.019 to 0.042 μg/ml
Fuel-mix tune up	3	<0.5 μg/ml	<0.5 μg/ml
Engine tune up	3	<0.003 μg/ml	<0.003 μg/ml
Gas power booster	3	0.009 μg/ml	0.008 to 0.010 μg/ml
Gas treatment	3	0.012 μg/ml	0.016 to 0.019 μg/ml
Gasoline antifreeze	3	0.007 μg/ml	0.006 to 0.009 μg/ml
Gas booster	6	0.051 μg/ml	0.008 to 0.096 μg/ml
Carburetor tune up	3	---	0.272 to 2.71 μg/ml
Motor oil	4	0.023 μg/ml	<0.004 to 0.08 μg/ml

5.1.2.4 Manganese as a Substitute for Lead in Fuels—The use of manganese compounds in fuels, principally as a smoke inhibitor, has been increasing. Currently around 450,000 kilograms of such additives are used per year, principally as smoke suppressants in residual-oil-fired stationary power plants, stationary gas turbines, and aircraft turbine overhaul facilities. One such compound, methylcyclopentadienyl manganese tricarbonyl (MMT), was introduced in 1958 as a supplemental antiknock material for use with tetraethyl lead (TEL). At the present time, MMT is receiving attention as a TEL substitute for use in the limited-lead/phosphorus fuels EPA regulations required by July 1, 1974.[17] Current use in gasoline, however, is very limited.

The following is a brief summary of information provided by the Ethyl Corporation, the developer of MMT as an additive for unleaded gasoline.[18]

> Use of MMT at the recommended maximum concentrations in gasoline (0.033 g/liter or 0.125 g/gal) provides, on the average, 2.5 road octane numbers which could represent a saving in crude oil of about 1 percent. The upper limit of MMT concentration is governed by engine durability problems at higher concentrations. Manganese in MMT is converted to Mn_3O_4 in the exhaust. Typically about 0.1 percent of the MMT is emitted from the tailpipe unburned. This rapidly decomposes in sunlight (in less than 2 minutes) with indications that the manganese is converted to a mixture of manganese oxide and carbonates. There is no evidence of the formation or presence of any manganese carbonyl compound. The organic portion of the solids appears to be a mixture of oxides, esters, and polymers.

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In tests conducted by Ethyl Corporation, benzo[a]pyrene (BaP) was reduced in exhausts when MMT was added. The use of MMT in test vehicles resulted in no significant differences in exhaust particulate concentrations. It is estimated that the size range of airborne manganese particles in the ambient atmosphere resulting from the use of MMT in gasoline would be the same as that of lead particles, i.e., 0.2 to 0.4 micron (mass median equivalent diameter). Using lead as a model, the use of MMT in gasoline would result in an increase of manganese concentration in urban atmospheres of 0.25 $\mu g/m^3$ or less. The use of MMT compared with clear gasoline in test vehicles did not adversely affect either regulated (HC, CO, and NO_x) or unregulated emissions. Tests conducted using exhaust from a car operating on fuel containing 0.125 g Mn/gal had no significant effect on the rate of oxidation of SO_2 in ambient air. In test car operations, MMT, compared to clean fuel, did not lessen the effectiveness of exhaust catalysts in oxidizing unburned hydrocarbon and carbon monoxide. Under extreme operating conditions some plugging of monolithic exhaust catalyst has occurred; however, rapid catalyst deterioration has been observed under similar operating conditions without the use of manganese additive.

The possibility of savings of 1 percent in crude oil by the use of MMT is very attractive. It raises the very fundamental question, however, of whether manganese is preferable to lead. A number of related questions must be answered before a definitive answer to the basic question is available. Estimates of manganese concentrations resulting from the use of MMT in gasoline must be confirmed, as must the estimated effects of MMT on other exhaust emissions. Further work also needs to be done on the effect of MMT on catalyst and vehicle operation. The manganese concentrations that would result from the use of MMT are estimated later with other concentration data in Section 5.2.1.4.

The Ethyl Corporation summary indicates there would be no significant difference between particulate emissions from clear fuels and fuels containing manganese. Tests sponsored by EPA, however, indicate that particulate emissions increase up to 100 percent when MMT is added to the fuel. Neither of the studies accurately characterizes the particulate matter physically and chemically. Size versus mass distributions were obtained in both studies, but size versus number distributions were obtained in neither. Since the manganese particulates tend to be confined to the submicron range, the number of particles emitted may be equally as important as the mass.

Present studies suggest that manganese exhaust particulate is very similar to lead exhaust particulate in size distribution and in percent emitted relative to that burned in the fuel. The mass median equivalent diameter is 0.1 to 1 μm, depending on mileage, driving cycle, etc. Unlike TEL, however, MMT does not require a scavenger (ethylene dichloride and ethylene dibromide for TEL) to remove its combustion products from the engine combustion chamber and exhaust manifold. Exhaust manganese particulate is principally Mn_3O_4 with traces of Mn_2O_3. Current data suggest that none of the parent manganese compound is exhausted. Typical exhaust particulate data for fuels with and without additives are shown in Tables 5.9 and 5.10.

Studies conducted by the Ethyl Corporation on the conversion of sulfur dioxide to sulfur trioxide suggest that manganese would have relatively little effect on the presence of sulfates. The importance of the sulfate and sulfuric acid problem, however, requires full evaluation of this aspect. The Ethyl Corporation tests were conducted in a 100-m^3 black polyethylene bag and the mixture was not irradiated.

The effect of manganese fuel additives upon nonregulated emissions from mobile sources (for example, polynuclear aromatic hydrocarbons, phenols, aldehydes, and oxygenates) is not known. Limited data suggest that manganese results in a reduction in the percentage of carbon in exhaust particulate (Table 5.10). Further work is also needed to ascertain the effect of manganese gasoline additives on regulated emissions (carbon monoxide, hydrocarbons, and nitrogen oxides).

The EPA fuel regulations requiring that a fuel of limited lead and phosphorous be available by July 1974[17] were based upon the fact that lead and phosphorus adversely affect the performance of exhaust catalytic control devices. Such devices will be used by most, if not all, of the domestic automobile manufacturers in model year 1975 and thereafter. The suggested use of manganese compounds as substitute antiknocks for

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Table 5.9. EFFECT OF MANGANESE FUEL ADDITIVE ON EXHAUST PARTICULATE[15,a]

Fuel	Vehicle number	Vehicle miles[b]	Exhaust particulate, g/mi[c]
91 octane clear	10	2,900	0.005
		4,250	0.004
		6,500	0.007
		8,600	0.007
		11,000	0.006
		13,000	0.008
		15,000	0.009
91 octane plus 0.25 g Mn/gal[d]	12	2,000	0.02
		4,000	0.02
		6,000	0.027
		8,400	0.022
		10,000	0.04
Commercial leaded regular	15	10,000	0.116
		10,360	0.094
	16	7,900	0.09
		8,260	0.11

[a]1972 Chevrolet 350 CID, 60 mi/hr cruise condition, air-diluted particulate collected on 142-mm glass fiber filter, 1-ft^3/min isokinetic-proportional sample. (1972 Chevrolet 5.7-liter displacement, 96 km/hr cruise condition, air-diluted particulate collected on 142-mm glass fiber filter, 28.3 liter/min isokinetic-proportional sample).

[b]Multiply by 1.6 to get kilometers.

[c]Multiply by 0.62 to get grams/kilometer.

[d]Multiply by 0.26 to get grams/liter.

Table 5.10. EFFECT OF MANGANESE FUEL ADDITIVE ON PERCENT CARBON IN EXHAUST PARTICULATE[19,a]

Fuel	Vehicle number	Vehicle miles[b]	Carbon in exhaust particulate, %	Exhaust particulate, g/mi[c]
91 octane clear	D-2547	6,917	43 to 48	0.04
		8,592	28	0.05 to 0.07
		10,739	72	0.04 to 0.06
91 octane plus 0.25 g Mn/gal[d]	D-2549	3,964	47	0.08
		5,975	18	0.09 to 0.16
		8,361	24 to 29	0.09 to 0.15

[a]1972 Federal Test Procedure,[20] 1972 Chevrolet 350 CID (5.7 liter displacement), cold start condition, air-diluted particulate collected on glass fiber filter.

[b]Multiply by 1.6 to get kilometers.

[c]Multiply by 0.62 to get grams/kilometer.

[d]Multiply by 0.26 to get grams/liter.

this fuel raises questions as to the effect of manganese on these devices. Limited studies indicate that manganese may be detrimental to the performance of certain such devices under specific operating conditions. More research on this problem is required.

5.2 CONCENTRATIONS

5.2.1 Air[21,22]

Few attempts have been made to evaluate the impact of major manganese sources on the ambient air in the immediate vicinity of these sources. Practically all data relating to the extent of manganese pollution have been acquired from studies aimed at the general definition of the nature and extent of air pollution on a national or, in a few instances, on a local scale. The number of major sources is relatively small, thus restricting somewhat the areas expected to have high levels of manganese in the air. Smaller sources are widespread; consequently, manganese would be expected to be present as a common pollutant in most atmospheres. The major portion of manganese emitted is in the form of smaller particles favoring wide distribution over considerable distances.

5.2.1.1 Manganese in Suspended Particulate Matter

5.2.1.1.1 NASN studies—Beginning in 1957, samples of suspended particulate matter collected at approximately 300 urban and 30 nonurban National Air Surveillance Network (NASN) sites have been analyzed for trace metals including manganese.[23,24] The spectrographic method employed in the analysis has sufficient sensitivity to detect manganese in practically all urban and in many nonurban samples, thus providing a broad data base.

The 1,000 station-years of data for urban and nonurban NASN sites for 1957-69 are summarized in Table 5.11 and the sites categorized into four different concentration ranges. All nonurban and a majority of urban sites fall into the lowest concentration interval. Except for the earliest period (1957-1963), there is a remarkable consistency in the distribution among the four concentration intervals. The deviation is understandable, since the 128 station-years of data obtained during the first 7-year period are from a relatively small number of sites and are not as representative as the data for subsequent years. The national annual average urban concentration is well below 0.20 $\mu g/m^3$.

NASN sites for which average concentrations have been 0.5 $\mu g/m^3$ or greater are listed in Table 5.12. Higher concentrations for shorter average times (quarterly and 24-hour) have been included to show maximum exposures, which may be of considerable significance in the evaluation of the potential biological effects of airborne manganese. The presence on this list of Johnstown, Charleston, and Niagara Falls is to be expected, as all are known to have ferromanganese or silico-manganese industries in the immediate areas. Both annual and maximum 24-hour averages for Johnstown were consistently high, apparently because source strength, location, topography, and meteorological conditions favor retention of pollutants in the air over the area. The high levels in Canton and Gary are no doubt related to the use of manganese products in the local steel industries. Sources of the high levels found in Philadelphia, Lynchburg, and Knoxville have not been discovered. Occasional elevated 24-hour values have been reported for other cities with annual average concentrations well below 0.5 $\mu g/m^3$: Cleveland, Ohio, 2.60; Cincinnati, Ohio, 2.80; Youngstown, Ohio, 2.10; Hammond, Indiana, 1.80; and East Chicago, Illinois, 1.70. Available data do not provide an adequate base for drawing valid conclusions with respect to long-term trends in ambient manganese concentrations.

Table 5.11. NUMBER OF NASN STATIONS WITHIN SELECTED ANNUAL AVERAGE MANGANESE CONCENTRATION INTERVALS, 1957-1969[23]

Year		Concentration interval, $\mu g/m^3$				Total
		<0.099	0.100-0.199	0.200-0.299	>0.300	
1957-1963	No. stations	76	29	10	13	128
	Percent	59.4	22.7	7.8	10.2	100
1964	No. stations	68	12	6	7	93
	Percent	73.1	12.9	6.5	7.5	100
1965	No. stations	132	14	5	6	157
	Percent	84.1	8.9	3.2	3.8	100
1966	No. stations	113	8	4	3	128
	Percent	88.3	6.3	3.1	2.3	100
1967	No. stations	121	13	4	4	142
	Percent	85.2	9.2	2.8	2.8	100
1968	No. stations	126	11	2	6	145
	Percent	86.9	7.6	1.4	4.1	100
1969	No. stations	169	23	9	8	209
	Percent	80.9	11.0	4.3	3.8	100
1957-1969	No. stations	805	110	40	47	1002
	Percent	80.4	11.0	4.0	4.7	100

Table 5.12. NASN STATIONS WITH ANNUAL AVERAGE MANGANESE CONCENTRATIONS GREATER THAN 0.5 $\mu g/m^3$ [23,24]

Year	Station	Manganese concentration, $\mu g/m^3$		
		Average	Max. quarterly	Max. 24-hr
1958	Charleston, W.Va.	0.61	1.10	7.10
1959	Johnstown, Pa.	2.50	5.40	7.80
	Canton, Ohio	0.72	1.10	2.20
1960	Gary, Ind.	0.97		3.10
1961	Canton, Ohio	0.57		2.90
	Philadelphia, Pa.	0.70		>10.00
1963	Johnstown, Pa.	1.44		6.90
	Philadelphia, Pa.	0.62		3.70
1964	Charleston, W.Va.	1.33		>10.00
1965	Johnstown, Pa.	2.45	3.90	
	Philadelphia, Pa.	0.72	1.70	
	Lynchburg, Va.	1.71	2.50	
	Charleston, W.Va.	0.60	1.70	
1966	Niagara Falls, N.Y.	0.66	1.30	
1967	Knoxville, Tenn.	0.81	1.50	
1968	Johnstown, Pa.	3.27		14.00
1969	Niagara Falls, N.Y.	0.66	1.30	
	Johnstown, Pa.	1.77	2.10	
	Philadelphia, Pa.	0.50	1.30	

5.2.1.1.2 Kanawha Valley study[25] — As part of a comprehensive air pollution study of the Kanawha River Valley in the vicinity of Charleston, West Virginia, conducted during 1964-65, 24-hour samples of suspended particulate matter were collected at 14 strategically located sites of a 27-station network (Figure 5.1). Sampling sites were placed from Falls View to Nitro, a distance of about 80 km (50 mi). Samples from selected sites were composited on a seasonal basis (fall 1964, winter 1964-65, spring 1965, summer 1965) and the composites analyzed for trace metal content by the NASN emission spectrographic procedure. The high concentrations of suspended manganese found at the Smithers and Cedar Grove sites are noteworthy (Table 5.13), as is the excessively high winter concentration at the Montgomery site; concentrations found at these sites far exceed those occurring at other NASN stations. The study report offers no clear explanation of the elevated manganese levels found, but it is quite obvious that the major source was the ferromanganese plant in the nearby Alloy area (Figure 5.1), with additional contributions from a large coal-burning industrial steam-generation plant in the same general area.

These Kanawha Valley data represent the only documented single-source study done in the United States. The impact of this source on the surrounding area is clearly shown by both the ambient air and settled manganese data (Figure 5.1 and Table 5.13). The fall and winter ambient air data dramatically demonstrate that, with favorable topography and meteorologic conditions, one strong source can exert an influence over a considerable distance. The Smithers and Montgomery communities have the highest seasonal manganese concentrations documented to date — 11 and 13 $\mu g/m^3$, respectively.

Figure 5.1. Location of fixed sampling stations in Kanawha River Valley. Average manganese concentrations ($\mu g/m^3$) for the study period (1964-1965) are indicated for selected sites.[25]

Table 5.13. MANGANESE CONCENTRATIONS, KANAWHA VALLEY AREA, 1964-1965[25]

Sampling site and number	Suspended particulates, μg Mn/m³					Settled particulates, mg Mn/m²-mo (study period average)
	Seasonal averages				Study period average	
	Fall 1964	Winter 1964-65	Spring 1965	Summer 1965		
Falls View (1)		3.40				
Smithers (5)	11.00	6.50	4.50	3.00	8.30	193
Montgomery (6)		13.00				27
Cedar Grove (7)	4.20	3.50	1.80	0.32	2.45	1.3
Marmet (11)		3.60				1.1
Kanawha City (13)	3.30	1.10	0.53	0.27	1.30	0.8
Charleston (15)		0.91				
West Charleston (17)		0.96				
North Charleston, West (19)		0.52				2.4
South Charleston, East (20)	2.00	0.26	0.23	0.17	0.67	3.2
Dunbar (22)		0.24				
St. Albans (24)	0.43	0.44	0.06	0.06	0.25	0.8
Nitro (25)	0.59	0.28	0.10	0.09	0.27	0.9
Nitro-West (27)		0.08				

5.2.1.1.3 Birmingham study[26] – Seasonal levels of trace metals were determined on suspended particulate matter samples collected at 10 Birmingham, Alabama, area sampling sites during 1964-65. No exceptionally high concentrations were discovered at any sampling site (Table 5.14); however, seven of the 10 sites would fall into the two highest concentration intervals of Table 5.11. Although a large steel plant was operating in the area during this study period, there is no evidence that any ferromanganese alloy was being produced concurrent with the sampling. In contrast to the Kanawha Valley situation, while the annual average levels for the truly urban sites ranked in the highest interval, no "hot spots" were uncovered during this study.

Table 5.14. MANGANESE CONCENTRATIONS, BIRMINGHAM AREA, 1964-1965[26]
($\mu g\ Mn/m^3$)

Place	Site	Seasonal averages				Study period average
		Spring	Summer	Fall	Winter	
Bessemer	1	0.21	0.18	0.15	0.11	0.16
Birmingham	3	0.33	0.35	0.35	0.18	0.30
Birmingham	4	0.82	0.50	0.58	0.95	0.71
Birmingham	5	0.45	0.72	0.45	0.20	0.46
Birmingham	7	0.69	0.35	0.12	0.45	0.40
Fairfield	1	0.36	0.21	0.15	0.10	0.20
Irondale	1	0.30	0.33	0.12	0.21	0.24
Mt. Brook	1	0.21	0.25	0.19	0.12	0.19
Tarrant	1	0.39	0.44	0.29	0.46	0.40
Vestavia	1	0.27	0.14	0.09	0.07	0.14
Average		0.40	0.35	0.25	0.29	0.32

5.2.1.1.4 Other studies–Rhodes et al.[27] employed the energy dispersive X-ray fluorescence technique to determine the trace metals in suspended particulate samples collected at 12 of the 38 Texas Air Quality Network Stations on the same day in June 1971. Concentrations were below the minimum detectable limit ($0.02\ \mu g/m^3$) at four of the 12 stations. At the other eight sites, concentrations ranged from 0.01 to 0.11 $\mu g/m^3$. In July 1971, similar samples were taken on 3 days at 17 stations in Corpus Christi. Most samples were below the minimum detectable level; the highest level found was only $0.08\ \mu g/m^3$. The objective of this study was to investigate an analytical technique rather than to delineate the extent of trace metal air pollution in Texas; consequently, the data must be considered inadequate in terms of defining air quality.

Brar et al.[28] employed neutron activation analysis to determine the trace metal content of samples of particulate matter collected April 4, 1968, at 20 sampling stations in Chicago and two in the suburban area. Concentrations of manganese on this particular day ranged from 0.10 to 0.90 $\mu g/m^3$ in the city, with an overall average of $0.45\ \mu g/m^3$. The highest concentrations were in the Loop and the industrialized southeastern areas. The results of this single day's sampling indicate that Chicago's average manganese pollution ranks in the upper 5 percent of the nation's urban areas.

A study was conducted some 40 years ago in the immediate vicinity of a manganese alloy plant located in Sauda, Norway.[8] Although the analytical method employed underestimated the manganese levels, the results show that ambient air concentrations in the area reached at least 65 $\mu g/m^3$ of manganese oxide or 46 $\mu g/m^3$ of manganese.

5.2.1.1.5 Size distribution of particulate manganese in the ambient air—Lee et al.[29] have determined the concentration of trace metals in quarterly composites of the different particle size range samples collected by means of cascade impactors operated at each of the six Continuous Air Monitoring Stations operated in conjunction with NASN. The particle size distribution data for manganese (Table 5.15) demonstrate quite clearly that at least 50 percent of the mass of suspended manganese is associated with particles having a Stokes equivalent diameter of 2 μm or less and that approximately 80 percent of the manganese is found in the respirable (< 5 μm) particle size range. These findings agree with reports indicating that much of the manganese emitted into the atmosphere is associated with particles in the 0.1- to 5-μm range.

5.2.1.2 Manganese in Settled Particulates—Very little information is available relative to the deposition on land and water of manganese from major sources. The Kanawha Valley Study data (Table 5.13) provide some indication of the amount of manganese deposited in the vicinity of a source of unknown magnitude (Smithers, Montgomery); in addition the data show that appreciable amounts may be deposited in industrial areas somewhat remote from known sources (North Charleston, South Charleston) with a high particulate deposition (dustfall) rate.

5.2.1.3 Manganese in Precipitation—Washout of manganese has been reported from the atmosphere at stations distributed throughout the United States.[30] Monthly composite samples of precipitation collected at each station during the period September 1966 to January 1967 were analyzed for manganese by atomic absorption spectrophotometry. The average manganese washout (Figure 5.2) ranged from below detectable at Mauna Loa, Hawaii; Amarillo, Texas; and the Tampa, Florida, airport to a maximum of 54 grams per hectare per month (g/ha-mo) at Caribou, Maine; with intermediate depositions of 31 and 26 at Midway and O'Hare airports (Chicago), respectively, and 23 at Sault St. Marie, Michigan. The high value for Caribou appears to be an anomaly, but it may result from the industrial megalopolis that is spread out in the upwind direction. The Albany, New York, data however, showing an average of 5 g/ha-mo, do not support this explanation. The Chicago airport data no doubt reflect industrial contributions, while the Sault St. Marie value is probably attributable to the ore handling and industrial activities in that area. The overall data indicate the widespread prevalence of manganese in the air over the whole of the United States. Because the majority of the stations were at relatively isolated sites with respect to major industrial areas, the data do not show the immediate influence of major sources.

5.2.1.4 Manganese from Mobile Sources—Section 5.1.2.4 indicated the use of manganese compounds in fuels is not very widespread at the present time, but may become more significant with the possible substitution of compounds such as MMT (methylcyclopentadienyl manganese tricarbonyl) for TEL (tetraethyl lead) as a primary fuel additive. The Ethyl Corporation[18] estimates that if these manganese compounds are used as a supplement in 50 percent of the gasoline used in the United States, the most that would be added to urban 24-hour air concentrations would be 0.05 to 0.2 μg Mn/m^3. This estimate assumed that the manganese emissions would be proportionate to the known lead emissions and distributions.

Manganese concentrations resulting from the use of MMT in gasoline were estimated independently by EPA and the Ethyl Corporation (Tables 5.16 to 5.22). Estimates were made for various distances from the edge of a 2-kilometer segment of a six-lane highway. Receptors were assumed perpendicular to the highway. Maximum hourly vehicle flow was assumed to be 12,000, and total 24-hour flow was 216,000.

Table 5.15. QUARTERLY AND ANNUAL SIZE DISTRIBUTIONS FOR SUSPENDED PARTICLES CONTAINING MANGANESE, 1970[29]

City	Quarter				Annual
	1	2	3	4	
Chicago, Ill.					
No. of samples	4	6	7	4	21
Avg. concentration, μg Mn/m³	0.03	0.04	0.04	0.03	0.03
Avg. mass median diameter, μm	2.02	1.86	2.03	1.75	1.91
Percent < 2 μm	50	53	50	55	52
Percent < 5 μm					80
Cincinnati, Ohio					
No. of samples	1	6	7	4	18
Avg. concentration, μg Mn/m³	0.01	0.31	0.30	0.19	0.17
Avg. mass median diameter, μm	1.42	2.16	2.24	2.16	2.14
Percent < 2 μm	63	46	44	46	47
Percent < μm					90
Denver, Colo.					
No. of samples	4	5	7	5	21
Avg. concentration, μg Mn/m³	0.01	0.02	0.02	0.03	0.02
Avg. mass median diameter, μm	1.37	1.34	1.90	2.25	1.75
Percent < 2 μm	64	64	52	45	55
Percent < μm					82
Philadelphia, Pa.					
No. of samples	2	6	7	5	20
Avg. concentration, μg Mn/m³	0.05	0.02	0.04	0.10	0.05
Avg. mass median diameter, μm	1.40	1.66	2.43	3.04	2.27
Percent < 2 μm	66	58	43	33	45
Percent < 5 μm					80
St. Louis, Mo.					
No. of samples	5	5	9	3	22
Avg. concentration, μg Mn/m³	0.04	0.03	0.04	0.02	0.03
Avg. mass median diameter, μm	2.01	2.23	2.36	2.20	2.20
Percent < 2 μm	50	46	43	47	47
Percent < 5 μm					73
Washington, D.C.					
No. of samples	5	6	6	6	23
Avg. concentration, μg Mn/m³	0.03	0.01	0.02	0.02	0.02
Avg. mass median diameter, μm	1.61	1.43	1.49	1.52	1.54
Percent < 2 μm	61	63	62	64	62
Percent < 5 μm					90

Figure 5.2. Manganese in precipitation (g/ha-mo), September 1966-January 1967.[40]

Table 5.16. ESTIMATED HOURLY MANGANESE CONCENTRATIONS, EPA MODEL

Vehicles using MMT, %	Distance from highway, meters	MMT = 0.125 g/gal			MMT = 0.057 g/gal		
		Max. conc., $\mu g/m^3$	Wind angle, degrees	Conc. with wind perpendicular, $\mu g/m^3$	Max. conc., $\mu g/m^3$	Wind angle, degrees	Conc. with wind perpendicular, $\mu g/m^3$
100	1	18	2	3.1	8.4	2	1.4
	10	11	4	2.8	5.0	4	1.3
	50	4.6	7	2.0	2.1	7	0.92
	100	2.8	11	1.5	1.3	11	0.69
	500	0.73	32	0.59	0.33	32	0.27
50	1	9.2	2	1.5	4.2	2	0.70
	10	5.5	4	1.4	2.5	4	0.64
	50	2.3	7	1.0	1.0	7	0.46
	100	1.4	11	0.76	0.63	11	0.35
	500	0.36	32	0.30	0.17	32	0.13
25	1	4.6	2	0.77	2.1	2	0.35
	10	2.7	4	0.70	1.2	4	0.32
	50	1.1	7	0.51	0.52	7	0.23
	100	0.69	11	0.38	0.31	11	0.17
	500	0.18	32	0.15	0.083	32	0.067

Table 5.17. ESTIMATED 24-hour MANGANESE CONCENTRATIONS, EPA MODEL

Vehicles using MMT, %	Distance from highway, meters	Concentration, $\mu g\ Mn/m^3$			
		MMT = 0.125 g/gal		MMT = 0.057 g/gal	
		With highway 81°-261°	With highway 111°-291°	With highway 81°-261°	With highway 111°-291°
100	1	3.4	1.7	1.5	0.79
	10	1.2	0.92	0.57	0.42
	50	0.26	0.53	0.12	0.24
	100	0.088	0.37	0.040	0.17
	500	0.021	0.10	0.0098	0.047
50	1	1.7	0.87	0.77	0.39
	10	0.62	0.46	0.28	0.21
	50	0.13	0.27	0.060	0.12
	100	0.044	0.18	0.020	0.084
	500	0.011	0.05	0.0049	0.023
25	1	0.85	0.43	0.39	0.20
	10	0.31	0.23	0.14	0.11
	50	0.065	0.13	0.030	0.061
	100	0.022	0.092	0.010	0.042
	500	0.0054	0.026	0.0024	0.012

Table 5.18. TRAFFIC VOLUMES AND METEOROLOGICAL CONDITIONS FOR 24 HOURS, EPA MODEL

Hour	No. vehicles, 10^3/hr	Wind directions, degrees	Wind speed, m/sec	Stability class	Mixing height
1	3.5	224	3.1	6	--
2	2	264	1.5	6	--
3	1.5	258	1.	6	--
4	1.5	261	1.	6	--
5	3	259	1.	6	--
6	7	261	1.	6	--
7	12	263	0.7	6	--
8	12	259	0.5	6	--
9	12	257	0.7	5	--
10	10.5	264	1.	4	745
11	10.5	260	1.	3	988
12	11	258	1.5	2	1231
13	11	259	1.	1	1474
14	11	259	1.	1	1717
15	12	171	2.6	2	1717
16	12	176	2.	3	1717
17	12	191	2.6	3	1717
18	12	194	2.6	4	1719
19	12	186	2.6	5	--
20	11.5	223	2.6	6	--
21	11	229	2.6	6	--
22	9	269	1.5	6	--
23	8.5	298	1.5	6	--
24	7.5	300	1.	6	--
Total	216				

Table 5.19. ESTIMATED HOURLY MANGANESE CONCENTRATIONS, ETHYL MODEL

Vehicles using MMT, %	MMT = 0.125 g/gal				MMT = 0.057 g/gal		
	Distance from highway, meters	Max. conc., $\mu g/m^3$	Wind angle, degrees	Conc. with wind perpendicular, $\mu g/m^3$	Max. conc., $\mu g/m^3$	Wind angle, degrees	Conc. with wind perpendicular, $\mu g/m^3$
100	1	2.42 to 3.63	3	0.64 to 0.99	1.10 to 1.65	3	0.29 to 0.44
	10	1.43 to 2.13	5	0.48 to 0.72	0.65 to 0.97	5	0.22 to 0.33
	50	0.67 to 1.00	9	0.20 to 0.31	0.31 to 0.45	9	0.09 to 0.13
	100	0.43 to 0.64	12	0.13 to 0.20	0.20 to 0.29	12	0.07 to 0.09
	500	0.12 to 0.17	34	0.09 to 0.15	0.05 to 0.08	34	0.04 to 0.07
50	1	1.21 to 1.83	3	0.32 to 0.48	0.56 to 0.83	3	0.15 to 0.23
	10	0.72 to 1.07	5	0.24 to 0.36	0.33 to 0.49	5	0.12 to 0.17
	50	0.33 to 0.51	9	0.11 to 0.16	0.16 to 0.23	9	0.05 to 0.07
	100	0.21 to 0.32	12	0.07 to 0.11	0.11 to 0.15	12	0.04 to 0.05
	500	0.07 to 0.09	34	0.05 to 0.08	0.03 to 0.04	34	0.03 to 0.04
25	1	0.61 to 0.91	3	0.16 to 0.24	0.28 to 0.41	3	0.07 to 0.11
	10	0.36 to 0.53	5	0.12 to 0.19	0.16 to 0.24	5	0.05 to 0.09
	50	0.17 to 0.25	9	0.05 to 0.08	0.08 to 0.12	9	0.02 to 0.04
	100	0.11 to 0.16	12	0.04 to 0.05	0.05 to 0.08	12	0.02
	500	0.03 to 0.04	34	0.03 to 0.04	0.01 to 0.03	34	0.01 to 0.02

Table 5.20. ESTIMATED 24-hour MANGANESE CONCENTRATIONS, ETHYL MODEL[a]

Vehicles using MMT, %	Distance from highway, meters	Concentration, $\mu gMn/m^3$	
		MMT = 0.125 g/gal	MMT = 0.057 g/gal
100	1	0.48 to 0.72	0.22 to 0.33
	10	0.36 to 0.54	0.17 to 0.25
	100	0.15 to 0.23	0.07 to 0.10
	200	0.10 to 0.15	0.05 to 0.07
	500	0.07 to 0.11	0.03 to 0.05
50	1	0.24 to 0.36	0.11 to 0.17
	10	0.18 to 0.27	0.09 to 0.13
	100	0.08 to 0.12	0.04 to 0.05
	200	0.05 to 0.08	0.03 to 0.04
	500	0.04 to 0.06	0.02 to 0.03
25	1	0.12 to 0.18	0.06 to 0.08
	10	0.09 to 0.14	0.04 to 0.06
	100	0.04 to 0.06	0.02 to 0.03
	200	0.03 to 0.04	0.01 to 0.02
	500	0.02 to 0.03	0.01 to 0.01

[a]Worst meteorological case, wind perpendicular to road.

Table 5.21. ESTIMATED MAXIMUM MANGANESE CONCENTRATIONS, ETHYL MODEL[a]

Vehicles using MMT, %	Distance from highway, meters	Wind angle, degrees	Concentration, μg Mn/m^3	
			MMT = 0.125 g/gal	MMT = 0.057 g/gal
100	1	3	1.82 to 2.73	0.83 to 1.24
	10	5	1.07 to 1.60	0.49 to 0.73
	50	9	0.50 to 0.75	0.23 to 0.34
	100	12	0.32 to 0.48	0.15 to 0.22
	500	34	0.09 to 0.13	0.04 to 0.06
50	1	3	0.91 to 1.37	0.42 to 0.62
	10	5	0.54 to 0.80	0.25 to 0.37
	50	9	0.25 to 0.38	0.12 to 0.17
	100	12	0.16 to 0.24	0.08 to 0.11
	500	34	0.05 to 0.07	0.02 to 0.03
25	1	3	0.46 to 0.68	0.21 to 0.31
	10	5	0.27 to 0.40	0.12 to 0.18
	50	9	0.13 to 0.19	0.06 to 0.09
	100	12	0.08 to 0.12	0.04 to 0.06
	500	34	0.02 to 0.03	0.01 to 0.02

[a]Worst meteorological case, maximum concentrations for least favorable wind angle.

Table 5.22. ESTIMATED STREET CANYON MANGANESE CONCENTRATIONS, ETHYL MODEL[a]

Vehicles using MMT, %	Distance from highway, meters	Concentration, μg Mn/m^3	
		MMT = 0.125 g/gal	MMT = 0.057 g/gal
100	1	0.84 to 1.26	0.38 to 0.57
	10	0.43 to 0.65	0.19 to 0.29
50	1	0.42 to 0.63	0.19 to 0.29
	10	0.22 to 0.33	0.10 to 0.15
25	1	0.21 to 0.32	0.10 to 0.14
	10	0.10 to 0.16	0.05 to 0.07

[a]Worst meteorological case, 1.5 meter elevation.

The mathematical models used to develop these estimates were based upon available roadside measurements for lead and carbon dioxide; a proportionality factor was used for computing manganese concentrations. It was assumed that 20 percent of the manganese in the gasoline would be emitted from the exhaust. Neither of the models has been validated. EPA is currently measuring carbon monoxide and sulfate concentrations in the vicinity of major freeways in California, and these data will provide a basis for validating the EPA model. Since current use of MMT is limited, however, the models cannot now be validated for manganese concentrations.

Since neither of the models has been validated, the estimates obtained cannot be considered significantly different. The EPA model, however, does predict maximum concentrations four to five times higher than the Ethyl model. The two models have not been analyzed in detail to determine the reasons for the difference. Some of this difference can be attributed to the fact that more stable meteorological conditions were assumed for the EPA model – conditions that would not be expected to occur more than once per year. Further, the EPA model does not consider the thermal effects due to the heat generated from the fuel burned. It is generally agreed that this factor would be significant in cases of slow-moving or stalled traffic, but there is a question concerning the relative importance of the thermal effects as compared with the turbulent wake effect when traffic is moving at reasonable speeds.

Based on the model estimates, the expected manganese concentration under worst conditions would be less than 5 $\mu g/m^3$ for a 24-hour averaging time. For comparison, the maximum average 24-hour manganese concentrations in 1968 in three large cities were: Washington, 0.09 $\mu g/m^3$; Los Angeles, 0.07; and Chicago, 0.26. Cities with major manganese emitting industries close by have significantly higher levels: Pittsburgh, 1.10 $\mu g/m^3$; Johnstown, 14.00; and East Chicago, 0.67.[24]

5.2.2 Water

The manganese in fresh water consists of dissolved and suspended salts. In the United States, most studies of the manganese in fresh water have determined the total amount of manganese in the sample, not individual compounds. In 1938, the surface waters of eight Wisconsin lakes were found to contain between 3 and 23 μg/liter. A more recent study of surface waters from lakes in Maine revealed concentrations varying from 0.02 to 87.5 μg/liter and a mean concentration of 3.8 μg/liter. Analysis of Mississippi River water at Fairport, Iowa, showed 80 to 120 μg/liter of manganese. The median manganese concentration of 52 samples from 15 large U.S. rivers was 20 μg/liter. Various investigators have found the concentration of manganese dissolved in sea water to vary between 0.4 and 10 μg/liter.

Manganese in the public water supplies of the hundred largest cities ranges from 0 to 2.5 milligrams per liter (mg/liter) for treated water. A U.S. Public Health Service (PHS) study of 969 community water supplies found a maximum concentration of 1.32 mg/liter of manganese at the consumer's *tap*; also, 211 of 2,595 samples exceeded the PHS Drinking Water Standard of 0.05 mg/liter.[30] The PHS Drinking Water Standard was established on the basis of aesthetic and economic considerations rather than physiological hazards.[31]

The manganese concentrations in a number of U.S. water systems are summarized in Table 5.23.[32] Based upon these values and assuming a daily water consumption of 2 liters, the daily ingested dose of manganese from drinking water would range from 6 to 100 μg/day.

Table 5.23. MANGANESE CONCENTRATIONS IN U.S. WATER SYSTEMS[32]

System	Concentration range, μg/liter	Detection, % of samples
Ohio River	6 to 30	17
Mississippi River	9 to 50	11
Columbia River	3 to 5	13
Great Lakes	5 to 5	4

5.2.3 Food

The manganese contents of foods are shown in Table 5.24.[33] In a more detailed listing,[8] nuts, tea, and spices contain the highest concentrations—35, 276, and 263 μg/g wet weight, respectively.

Table 5.24. MANGANESE CONCENTRATIONS IN GROUPS OF PRINCIPAL FOODSTUFFS[33]

Class of food	Manganese concentration, μg/g (wet weight)
Grains and cereals	1.17 to 30.76
Dairy products	0.00 to 1.88
Meat and poultry	0.00 to 0.75
Fish and seafood	0.00 to 0.12
Fruit	0.20 to 4.68
Nuts (edible part only)	0.38 to 35.09
Vegetables	0.24 to 12.74
Condiments and beverages	0.00 to 275.58
Fats and oils	0.00 to 4.95

5.2.4 Soil

Manganese is considered to be the 12th most abundant element in the earth's crust. It is found in igneous, sedimentary, and metamorphic rocks. Igneous rocks have been reported to contain 950 μg/g, shales 850 μg/g, sandstones 50 μg/g, and limestones 1100 μg/g. Most important from an environmental point of view is the distribution of manganese in the soil. The concentration depends on the parent rocks from which the soil was formed and the amount of manganese they contained (Table 5.25).[34]

Table 5.25. MICRONUTRIENT CONCENTRATIONS IN SOILS AND ROCKS[34]
(μg/g)

Element	Earth's crust	Basic rocks	Acid rocks	Sedimentary rocks	Soils
Boron	10	10	15	12	10
Manganese	1,000	2,000	600	670	850
Iron	50,000	86,000	27,000	33,000	38,000
Cobalt	40	45	5	23	8
Copper	70	140	30	57	20
Zinc	80	130	60	80	58
Molybdenum	2.3	1.4	1.9	2	2

Soils have an average manganese content of 800 to 850 μg/g.[8] Manganese in the soil is found in a water-soluble form in the soil solution, in the exchangeable Mn^{2+} as organically bound manganese, and as various manganese oxides. The amount of manganese in solution, as well as on the exchange complex, is very low in alkaline soil. A dynamic equilibrium is thought to exist between the manganese in soil solution, adsorbed on the exchange complex, and the precipitates of higher oxides or hydroxides.[35]

Manganese cycles in the soil have been postulated. In these cycles, divalent manganese (Mn^{2+}) is transformed through biological oxidation to the less-available trivalent form (Mn^{3+}); later through dismutation, the Mn^{3+} is reduced biologically to Mn^{2+}. A dynamic equilibrium exists between all forms.[36] The oxidizing power of higher oxides increases with acidity; therefore, reduction by organic matter is more likely at low pH values. If the oxygen tension is low, biological reduction can take place at any pH value. Bacterial oxidation is very slow or absent in very acid soils, and Mn^{2+} predominates since organic matter can reduce the higher oxides. In alkaline soils, the Mn^{2+} nearly disappears; bacterial oxidation is rapid and reduction by organic matter is slow. In well-aerated soils above a pH of 5.5, soil microorganisms can oxidize the Mn^{2+} rapidly.[37] The rate of exchange between the various forms is not known at the present time.

The solubility of manganese is markedly affected by microbial process. Microorganisms are active in catalyzing both the oxidations and the reductions in which manganese is precipitated or solubilized. These microorganisms are spread universally throughout the biosphere and are probably important in precipitating the manganese found in sediments. Under anaerobic and reducing conditions, sulfate-reducing bacteria precipitate manganese. The availability of manganese in the soil may be affected by microorganisms in the following ways:

- Release of inorganic ions during decomposition of organic material.
- Immobilization of ions by incorporation into microbial tissue.
- Oxidation of manganese, generally to a less available form.
- Reduction of an oxidized form of manganese under conditions of limited oxygen tension.
- Indirect transformation through changes in pH or oxidation potential.[38]

Manganese in soil exhibits a very pronounced seasonal variation. This is probably due to oxidation and reduction induced by microbial action.[34] Summer seems to favor the manganous (Mn^{2+}) form and winter the manganic (Mn^{3+}) form, though the opposite is said to be true in alkaline soils. Tisdale and Bertramson[39] have indicated that a relationship between elemental sulfur and manganese exists and influences the availability of manganese.

5.2.5 Biological Tissues

Under average environmental concentrations of manganese, terrestrial mammals concentrate available manganese up to a factor of 10, whereas marine plants and fish concentrate it by factors of 100,000 and 100, respectively. The average manganese concentration for terrestrial mammals may be as high as 1.0 μg/g wet tissue.[8] Tissue concentrations of manganese range from 0.2 μg/g in muscle to 3.3 μg/g in bone, with an average of from 0.2 to 0.3 μg/g wet tissue.[8] In addition to bone, tissues showing high levels of manganese are liver (2.5 μg/g), pituitary (2.5 μg/g), pancreas (1.9 μg/g), and kidney (1.2 μg/g).[8]

In humans, approximately 10 percent of the average daily dietary intake of manganese is absorbed through the gastrointestinal tract. Manganese absorption through the gastrointestinal tract is correlated with the available iron and the iron balance in the body. When an adequate amount of iron is available, manganese uptake is minimal, but when the iron supply is insufficient, manganese uptake is increased. This may be of concern to pregnant women and to undernourished groups because the resulting physiological anemia would promote gastrointestinal manganese uptake.

Manganese uptake in the lung is more efficient than that through the gastrointestinal tract by a factor of 3. An average size man (70 kg) inhaling an atmosphere that contained 5 mg/m^3 would absorb approximately 0.5 mg/g wet tissue per day.

5.2.6 Estimate of Daily Human Exposure

Only small segments of the population are exposed to manganese levels in excess of the current Threshold Limit Value for industrial exposure (5 mg/m^3 for 8 hours) for air or in excess of the PHS Drinking Water Standard (0.05 mg/liter). Those directly involved in manganese mining and refining operations or living near production facilities for ferromanganese, steel, aluminum, copper, alloys, and voltaic cells may be exposed to higher levels.

The daily intake for nonoccupationally exposed individuals will vary widely, depending primarily upon the diet. Intake from food is much greater than that from inhalation or the ingestion of water. Schroeder et al.[33] estimate the daily background dose of manganese to be about 3000 μg/day (Table 5.26). Although the average intake of manganese from inhalation is small in comparison with that from food, in the cases of occupational exposure, it appears to be the major route of absorption.

Table 5.26. ESTIMATED DAILY BACKGROUND DOSE OF MANGANESE[33]

Exposure	Dose, μg/day
Inhalation	2
Ingestion	
Food	3,000
Water	5

5.3 TRANSPORT AND MODELING[8]

No transport model exists to describe the global distribution of manganese. Such a model is required to determine a mass balance for manganese in order that emissions into the environment can be related to the various transformations in the total manganese cycle. The model should be able to account for the present levels of manganese, and must be able to predict the impact, including long-term effects on the environment, that may be caused by a change in input.

A necessary input into the model will be the rates of emission of manganese compounds into the environment. While the major paths by which manganese enters the environment are known, the total loss of manganese by the various escape routes is unknown. Accurate and up-to-date measurements on particle size, the rate of loss of these substances into the environment, and the distribution of emissions within the environment are needed before manganese compounds can be modeled.

The major sources of manganese in the atmosphere are manganese alloy, steel, and iron production. Minor sources are wind-blown soil, auto exhaust, mining operations, dry-cell battery production, fertilizers, fungicides, and synthetic manganese oxide production. The manganese compounds emitted from these sources can be classified as either fume or dust.

In manganese alloy production, 20 percent of the particles emitted have diameters greater than 20 μm, and 80 percent of the solids present in the gas as it leaves the furnaces is a typical fume, with particle sizes ranging between 0.10 and 1.0 μm. Similar size particles are produced in the iron and steel industries. Fly ash particles from oil-burning boilers range from less than 0.01 to 20 μm, depending on the degree of atomization of the oil, mixing efficiency, flame temperature, firebox design, flue gas path through the boiler to the stack, and number of collisions between fly ash particles. Manganese particles emitted by the combustion of manganese fuel additives will be in a size range less than 0.1 μm.

Considering the sources and size distribution of manganese, prevailing winds will be the main transport mechanism. Therefore, manganese particles will be deposited on land or water by gravitational settling and diffusion, washout, or rainout. If these removal mechanisms are dominant, the atmospheric residence time of manganese-containing particles will depend greatly on size and the amount of atmospheric precipitation. The large particles will be deposited near the source, and only the fine particles will be transported to remote areas.

Possible sources of soil contamination include aerosols, pesticides, limestone and phosphate fertilizers, manures, sewage sludge, and mine waste--all of which can add to the manganese burden of fresh water and sea water. Reentrainment of dust and soil containing manganese has not yet been studied.

Once transport mechanisms have been developed for manganese, it will be necessary to determine the ultimate fate of the degradation products in order to model this pollutant. The following six transformation and removal processes should be considered for manganese.

5.3.1 Dissolution in Fresh Water and Sea Water

All waters contain manganese derived from soil and rocks. Seawater manganese is found mostly as MnO_2, some of which can be explained by earlier observations that several genera of bacteria common to soils and ocean muds precipitate manganese oxides from manganese salts.

5.3.2 Rainout and Washout

Sampling for six metals at 32 stations in the United States indicates that manganese in atmospheric precipitation is derived primarily from human activity.[40]

5.3.3 Microbiological Utilization at Earth's Surface

In addition to the soil and ocean mud bacteria mentioned above, bacteria have been considered to be an agent in the formation of bog manganese ores. Recent research has demonstrated that manganese can be separated from refractory manganiferous materials by the action of by-products formed as a result of microbial metabolism.

5.3.4 Uptake by Soil and Plants

Plants apparently absorb manganese primarily in the divalent (Mn^{2+}) state.[8] Lowering the soil pH or reducing soil aeration by flooding or compaction favors the reduction of manganese to the Mn^{2+} state and thereby increases its solubility and availability to plants. Heavy fertilization of acid soils without liming–particularly with materials containing chlorides, nitrates, or sulfates–may also increase manganese solubility and availability. The availability of soil manganese is closely related to the activities of microorganisms that alter pH and oxidation-reduction potentials. Under some conditions of pH and aeration, the addition of organic compounds to soil can increase the chemical reduction of manganese and its uptake by plants. Although manganese and iron metabolism appear closely related in plants, the two elements behave differently–iron binds largely to citrate and moves as an anion, but manganese acts as a cation and does not bind with citrate.

5.3.5 Photochemical and/or Thermal Reactions in Lower Atmosphere

Sulfur dioxide, emitted into the atmosphere in the presence of sunlight and water vapor, is converted to sulfur trioxide and then to sulfuric acid. Ammonia or some metal compounds, including those of manganese, can promote this reaction. At the manganese concentrations normally present in the ambient atmosphere, the oxidation of sulfur dioxide resulting from the presence of manganese is not expected to be significant. Ammonia in the air is probably the rate-controlling factor in atmospheric sulfur dioxide oxidation.

Manganese dioxide reacts with nitrogen dioxide in the laboratory to form manganous nitrate, which is toxic. There is the possibility of such a reaction occurring in the atmosphere; however, it has not been observed.

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6. BIOLOGICAL EFFECTS

6.1 EFFECTS ON MAN AND LABORATORY ANIMALS

6.1.1 Introduction

Manganese is an essential trace element in all living things and is ubiquitously distributed in nature.[1,2] One of its major functions appears to be as a coenzyme in various metabolic processes, localized mainly in the mitochondria. While in trace amounts manganese is beneficial, industrial exposure of man to various manganese compounds has been associated with two different clinical pictures: chronic manganese poisoning affecting the central nervous system and a manganic pneumonia.

Manganese poisoning is a hazard in the mining and processing of manganese ores and in the use of manganese alloys in the steel industry, and in chemical industries. In manganese mining, dry high-speed drilling produces dust containing a large percentage of manganese dioxide; this, coupled with poor ventilation, provides the setting for most of the cases of chronic manganese poisoning reported in the literature, although other sources are known.[3]

Chronic manganese poisoning can result from exposure to high concentrations of manganese dust after only a few months, although it usually results from exposures of two to three years. Manganese may be absorbed by inhalation, ingestion, or through the skin. Most effects appear to result from prolonged inhalation, although some studies have shown that a greater amount of the metal enters the body by means of the intestinal absorption route. The damage produced is reversible if the patient is removed from exposure, but a sensitivity can evidently develop since persons who have recovered seem to be prone to contracting the illness again.

Acute manganese poisoning is extremely rare. Chronic exposure is seldom fatal but may result in permanent crippling. Diagnosis is difficult unless a history of exposure for at least three months is present. The symptoms are sleepiness, muscular twitchings, cramps in the legs, increased tendon reflexes, a peculiar characteristic spastic gait, emotional disturbances, and a fixed mask-like expression. Exposure to manganese dust has produced croupous pneumonia which frequently affects only one lobe of the lung. There is a high mortality rate from the pneumonia.[4]

6.1.2 Metabolism

Extensive reviews by Cotzias and coworkers[1,5] provide much of the understanding of manganese metabolism including absorption, excretion, turnover rates, and tissue profiles. Manganese metabolism is regulated by the adrenal glands. Ingested manganese is absorbed through the intestine and is concentrated in the liver. Manganese accumulates in organs rich in mitochondria and is selectively concentrated within mitochondria.[6] Although some may be distributed to the tissues, most of the excess metal is discharged via the bile or by other gastrointestinal routes, thereby keeping the manganese profile among various tissues relatively stable. A small percentage of the manganese excreted to the intestine is reabsorbed and is transported in the plasma in its trivalent form. Mahoney and Small[7] identified fast and slow components of the manganese disappearance curves that had respective half-times of 4 days and 39 days in humans. They found the biological half-time to be influenced by intake of manganese, amount of iron in storage, and hemoglobin concentration in the blood. They reported a half-time of 10 to 15 days in rats; this is supported by the work of Moore et al.[8], who found that the retention times of ^{54}Mn were similar when the source

was either $MnCl_2$ or MMT (methylcyclopentadienyl manganese tricarbonyl). The inorganic form, however, was excreted almost exclusively in the feces, while the organic form was excreted both in feces and in urine.

Skeletal structures, hair, liver, pancreas, and kidney contain concentrations of manganese that are characteristic of those tissues but that vary little among species. Generally, organs and tissues do not accumulate large concentrations of manganese.

Alstatt et al.[9] have shown that manganese and iron metabolism are closely related. The high degree of individual susceptibility of miners to chronic manganese poisoning has resulted in attempts by several investigators to relate it to nutritional deficiencies, specifically iron-deficiency anemia. Mena et al.[10] state that there is a proportionality between the intestinal absorption of iron and manganese in man and animals. Furthermore, it has been shown that anemia leads to an increased absorption of both iron and manganese. Chronic exposures to high levels of manganese increase hemoglobin values and erythrocyte counts, which indicates that manganese stimulates production of erythrocytes, as does iron-deficiency anemia. Recovery from anemia caused by improper nutrition is much prompter following the administration of ferrous sulfate and manganese chloride than of ferrous sulfate alone, which demonstrates the relationship between the effect of manganese on erythrocyte production and the intestinal absorption of manganese in anemic individuals.

6.1.3 Toxicological Effects

The toxicity of specific manganese compounds appears to depend upon the type of manganese ion present and the oxidation state of the manganese; the divalent manganese cation is reported to be two and one-half to three times more toxic than the trivalent cation. While most oxides are toxic to rats, the higher valence oxides are more toxic than the lower ones.

Table 6.1 summarizes the results of several studies of the effects of acute manganese excess in rats.

Table 6.1. EFFECTS OF ACUTE EXCESS OF MANGANESE INJECTED SUBCUTANEOUSLY IN RATS

Dose of manganese, mg/kg body wt	Time elapsed when effect noted, hr	Effect	Reference
50	10	Increase in hemoglobin and hematocrit.	11
53 to 60	4	Reduced bile flow rate, changes in liver ultrastructure characteristic of reduced bile flow.	12
53 to 60	24	Bile flow higher than controls. Ultrastructural changes not as severe as at 4 hours.	12
150	20	Increase in hemoglobin, hematocrit, mean corpuscular volume, serum chloride, phosphorus, and magnesium. Decrease in serum calcium and iron.	11
300	12 to 18	Maximum increase in hemoglobin and hematocrit.	11
170 or more	18	Necrotic changes in hepatic tissues.	11
300	48	Apparent increase in iron content of spleen and liver.	11

Male rabbits intra enously injected with 1.1 to 1.5 mg $MnCl_2$/kg body weight for up to 32 days showed hyperactivity after the first week but later became hypoactive.[13] There were tremors of the head and legs at the end of the exposure period. Pathomorphologic changes were greatest in the liver and least in the kidneys and intestine. The liver was necrotic and inflamed and had an appearance similar to that found in acute cirrhosis.

Hysell et al.[14] conducted studies with rats to determine the morphologic changes and tissue concentrations of manganese that occurred following oral intubation (stomach tube) of the fuel additive, MMT. Dosages varied from 15 to 150 mg/kg body weight. Deaths that occurred took place within 6 days after exposure; survivors appeared normal at 14 days. The LD_{50} after 14 days was 58 mg MMT/kg body weight. The manganese concentrations in tissues from animals dying after exposure depended on the dose and were rather high. At 14 days after ingestion, the manganese concentrations in survivors had decreased to approximately the normal range. There was no way to determine whether the observed toxicity was related to the intact MMT molecule or to some metabolite of the compound. It is apparent, however, that the toxic effects observed were not the result of acute manganese toxicity since acute toxicity occurs at much higher dosage levels than those used and since the pattern of hepatic lesions observed in these animals was markedly different from that seen in acute toxicity. The presence of high levels of manganese in the tissues, along with histopathological changes, suggests that the manganese was transported there as a metabolic product of the MMT. In addition, the occurrence of high levels of manganese in organs that normally have a low manganese content supports this hypothesis.

Moore et al.[15,16] exposed golden hamsters and albino rats for 8 hours per day for 56 days to automotive engine exhaust that contained about 0.12 to 0.13 mg Mn/m^3 (the manganese resulted from the addition of MMT to the gasoline). No gross changes in general conditions or appearance were observed in any of the animals. No gross abnormalities were noted in any of the hamsters or rats except for the usual chronic respiratory disease lesions in the rats. Microscopic examination of the tissues from the hamsters showed minimal changes related to exposure to exhaust emissions but no changes that could be related specifically to the presence of MMT.

A study in which cerebral tissues were examined by Jonderko and Szczurek[17] led to the conclusion that manganese poisoning directly affects functional parts of the brain; however, local circulatory disturbances also may produce changes in the central nervous system. Chandra and Srivastava[18] gave rats 8 mg $MnCl_2$/kg intraperitoneally for 180 days and found that the occurrence of degenerated neurons was maximal when the manganese concentration in brain was at a maximum; thus, the extent of damage to brain cells appears to be directly related to the amount of manganese in the brain..

Borisenkova[19] compared the effects from inhalation of dusts containing ferromanganese, silicomanganese, manganese dioxide, or iron oxide in rats exposed to 70 to 150 mg/m^3 for 4 months. The motor reflex, as indicated by the response of hind limb muscles, was affected between 7 and 12 weeks after the beginning of exposure to ferromanganese, after 12 to 15 weeks exposure to manganese dioxide, and after 15 to 16 weeks exposure to silicomanganese. Iron oxide produced no changes compared to controls. Changes in morphology of the brain were consistent with changes seen in the motor reflex, so that the primary effect appeared to be exerted on the central nervous system. After 4 months of inhalation, rats contracted interstitial chronic pneumonia from exposure to any of the compounds, including iron oxide.

6.1.4 Mechanisms of Manganese Poisoning

Brain function is dependent upon the transmission of nerve impulses between nerves to affect a certain end-organ response such as muscle contraction. Four chemicals function in the transmission of nervous impulses (dopamine, norepinephrine, serotonin, and acetylcholine). Furthermore, there is variable distribution of these neurotransmitters in specific structures of the brain. The regional localization of these neurotransmitters is significant because the normal functioning of the brain is controlled by excitatory (norepinephrine and dopamine) and inhibitory (serotonin) neurons and because regions high in various concentrations may be classified as inhibitory or excitatory.

Many of the symptoms of chronic manganese poisoning are similar to Parkinson's disease and both have as the basis of their symptomatology the abnormal function of the extrapyramidal system of the brain.[4] This system is associated with gross, coordinated movements of large parts of the body involving control of simultaneous contraction and relaxation of many different muscles. Normal functioning of this motor system depends upon a balance of two "antagonistic" groups of neurotransmitters.

Manganese can affect oxidative enzyme systems whose integrity is needed to continue to supply the energy required for the degradation and synthesis of the various chemical compounds that function in nerve transmissions.[20] Mandell and Spooner[21] have shown that alteration of these compounds may influence behavior, which is noteworthy in view of the behavioral symptoms of the intermediate phase of chronic manganese poisoning. Klawans[22] states that both Parkinson's disease and chronic manganese poisoning have as their basis unantagonized excitation of certain nerve centers because dopamine production is reduced as the result of a nerve tract lesion.

In a study of mutagenesis, Buttin and Kornberg[23] mentioned that processes such as genetic recombination might be affected by manganese via its influence on enzymes that control the structure and metabolism of the genetic material, deoxyribonucleic acid (DNA). The subcellular structure of ribosomes is dependent upon divalent cations, usually magnesium; but manganese can be substituted for magnesium in both the binding together of the two ribosomal subunits and the binding of messenger ribonucleic acid (RNA) to the whole ribosome.

6.1.5 Community and Occupational Exposure

Numerous instances of manganese intoxication have been reported since the disease was first recognized in 1837 by Couper. Initially, the disease was recognized in individuals working in manganese ore mills, battery factories, and the iron and steel industry, but most of the more recent cases of manganism have involved manganese miners. The disease is characterized by psychomotor disturbances, emotional instability, restlessness or apathy, hallucinations, flight of ideas, compulsory acts, and verbosity. Neurological symptoms such as weakness, excess salivation, and headaches are consistent features of the illness as well. Neurological signs of the disease include muscular tension, mask-like expression, gait disturbances, monotonous speech, tremor, and various sensory changes.

Airborne manganese-containing dust is implicated as the cause of manganese intoxication "by the observations that the time of onset of manganism is inversely related to the concentration in the air of the agent, and that, in rough terms, the severity of the disease is apt to be directly related to this concentration."[24] However, neither the particle-size distribution of the manganese dust nor the dose of manganese dust that can cause manganism is known.

6.1.5.1 Community Exposure–One epidemic of manganese intoxication in Japan was caused by well-water contaminated by manganese and zinc leached from discarded batteries.[25] Observed symptoms included loss of appetite, constipation, mask-like expression, excess salivation, painful leg joints, tremor, transient double vision, memory loss, and melancholia. One patient died, and large quantities of manganese and zinc were found in the organs examined at autopsy. Although the total doses of manganese consumed by the intoxicated individuals were not known, analysis of the well-water revealed 14 mg of manganese tetroxide per liter.

Managanese has been implicated in the pathogenesis of lobar pneumonia. Following the opening of a ferromanganese smelting plant in Sauda, Norway, in 1923, an increased incidence of lobar pneumonia was noted in workers in the plant and in the townspeople.[26] At first it was thought that this community was experiencing an epidemic of unusually virulent pneumonia, but the situation remained unchanged for many years without subsiding. Subsequent investigations[27-29] showed that:

- Mortality from pneumonia in Sauda was eight times that of the rest of Norway.
- The number of cases of pneumonia and deaths from pneumonia varied with the amount of manganese alloy produced at the plant.
- Infection rates and types of pneumococci were normal in all parts of the community—only the pneumonia morbidity and mortality rates were high.
- Smoke near the plant contained 54 percent silica and 2.56 percent manganese oxide.

Concentration of manganese in the atmosphere of Sauda reached a maximum of 64 $\mu g\ Mn_3O_4/m^3$, which corresponds to 46 $\mu g\ Mn/m^3$, at a point 3 kilometers from the plant. However, the method used to analyze for manganese was later found to give low results. The dose of inhaled manganese was not known.

A similar community situation in the vicinity of another ferromanganese plant in Aosta, Italy, was reported by Povoleri,[30] but was not subjected to as detailed study. Both the Norwegian and Italian communities were situated in deep, narrow valleys, which suffered from severe air stagnation and pollution, particularly in winter.

In addition to the above, excess illness and death from pneumonia frequently has been reported in other manganese industries in Europe. Of particular interest are the reports of Davies,[31,32] who made observations in England in a factory producing permanganates under very unfavorable wartime working conditions. The particle size of the dust was very small, which favored pulmonary deposition. In addition to noting an excess of pneumonia, Davies observed that other less serious respiratory illnesses—for example, bronchitis and pharyngitis—were above expected frequency. He reached the conclusion that manganese, at least in very fine particles, could both enhance the severity of infection and produce chemical pneumonitis, bronchitis, and pharyngitis.

Two recent Japanese reports[33,34] describe careful studies conducted by Kanazawa University medical faculty on school children located at different distances from a ferromanganese plant. Manganese dustfall measured monthly for 3 years averaged about 200 kilograms per square kilometer per month (kg/km^2-month) in the vicinity of the plant, compared with 8 kg elsewhere in Kanazawa. Total dustfall and sulfation rates were similar for all parts of the city. Some 24-hour suspended particulate measurements made in the plant neighborhood out to 300 meters showed levels from 4 to 260 $\mu g\ Mn/m^3$. These results are too meager to judge critical exposure level. Students in the junior high school 100 meters from the plant had higher prevalence of nose and throat symptoms, higher history of pneumonia, and lower pulmonary function than did students in a similar school in another part of the city remote from the manganese plant. In the students of the exposed school, pulmonary function was lowest in those with longer residence in the area and in those who lived closer to the factory. Following this study, controls were installed in the ferromanganese plant over a period of several months. These measures reduced the manganese dustfall from 200 to 20 kg/km^2-month. A resurvey of the two schools showed no change in the control school. Prevalence of nose and throat symptoms in the polluted school decreased to a level comparable to that of the control school. Lung function of children in the polluted school was also improved and similar to that in the control school, except in the oldest group of boys who still showed some deficit. These two studies have apparently bracketed a level of environmental manganese at which health effects begin to appear. The effects identified are apparently mainly reversible. The critical level is, however, not well identified in a quantitative sense.

Suzuki[35] made observations on pneumonia morbidity in another part of Japan. He found higher history of pneumonia rates in school children and their families near a ferromanganese plant than in a control group not so exposed. Primary schools were used, and the data were not separated by age groups. Similar differences in pneumonia history were found in groups of workers employed in the polluting factory or residents living nearby, as compared to suitable control groups. A study now underway in Yugoslavia[36] has also noted higher pneumonia morbidity in workers employed in a ferromanganese plant and in an adjacent

electrode plant when compared with a remote aluminum fabricating plant with very low manganese exposure.

6.1.5.2 Occupational Exposure to Manganese–Manganese poisoning, as discussed earlier in this chapter, is a hazard in mining and processing manganese ores, and in use of manganese alloys in the steel industry and manganese compounds in chemical industries. It is attributable primarily to exposure to dusts containing manganese dioxide. Over 400 cases of chronic manganese poisoning have been described, and the clinical symptomatology has been the subject of several reviews and numerous case reports.[37,38] Chronic manganese poisoning can be caused by exposure to high concentrations of manganese dust for only a few months, although onset of symptoms usually occurs after 2 to 3 years of continuous exposure. Poisoning follows a slow progressive course. Cotzias[5] has described three phases of chronic manganism: the prodromal period, the intermediate or psychiatric phase, and the period of severe neurological disorders. A significant aspect of chronic manganese poisoning is marked individual susceptibility to the disease, since many miners are exposed to manganese dusts but only a small percentage develop symptoms. Individual susceptibility may be related to individual variations in the excretory capacity of the liver and kidney which may lead to accumulation of toxic levels of manganese.[4] Liver lesions and a decreased bile flow rate as results of manganism have been reported by Witzleben.[12]

6.1.5.3 Clinical Diagnosis–There is no specific diagnostic test for chronic manganese poisoning, although measurement of urinary manganese concentrations has some value. The normal urinary concentration is 8 to 10 μg/liter and reflects the general level of exposure to manganese. Urinary concentrations, however, do not correlate well with the clinical severity of the symptomatology associated with manganism. Blood levels of manganese provide little clinical information, and blood urea nitrogen, fasting blood sugar, enzymes, and electrolytes are usually normal. Rodier[4] mentions diminished excretion of 17-ketosteroids in 81 percent of his patients, and changes in the relative concentrations of white blood cells in 52 percent. Furthermore, he reports an increased basal metabolic rate in 57 percent. Manganese content in hair was decreased by about 70 percent in his patients with chronic manganese poisoning. Kesic and Hausler[39] found increased hemoglobin values and erythrocyte counts and decreased monocyte counts. Cotzias[5] reported that cerebrospinal fluid tends to show a slight increase in cellular and protein content with manganese poisoning.

6.1.5.4 Pathology–There have been only four documented reports[40-43] of pathological changes in man from manganese exposure. One case involved advanced cirrhosis of the liver. All four cases involved degeneration of nervous tissue in the brain.

Pentschew states that the neuropathological findings in monkeys and cats showed such striking similarities with those in human cases of manganese encephalopathy that they could be said to be identical.[44]

6.1.5.5 Treatment of Chronic Manganese Poisoning–Treatment of chronic manganese poisoning has recently undergone a basic change that reflects a better understanding of the pathophysiology of the condition. Early attempts using various chelating agents; primarily ethylenediamine-tetraacetic acid (EDTA), were contradictory but did seem to produce some improvement in the condition if used in the early phase of poisoning when, presumably, neurons had not yet been destroyed. After structural neurological injury, no improvement could be expected. The results of Penalver[45] and Tepper[46] confirmed this and regarded treatment with chelaters as ineffective. Whitlock et al.[47] reported that treatment with intravenous calcium-EDTA mobilized body deposits of manganese, as evidenced by increased urinary manganese levels, and led to improvement in muscle strength and coordination within two to three months after treatment. Wynter[48] had poor results with EDTA in seven cases of advanced manganese poisoning but encouraging results in one patient with symptoms of the early stages. The essentially negative results should be expected, inasmuch as crippled ex-miners no longer exposed to manganese dust apparently clear the manganese overload that produced their neurological damage and its symptoms, even though the damage itself is not reversible.[49] Consequently, in the absence of appreciable manganese pools, chelating agents could not be expected to have any effect. Only in healthy miners still exposed to manganese should tissue manganese levels be sufficiently high to be amenable to chelating agents.

Recognizing that a similar biochemical defect was present in Parkinson's disease, Mena et al.[50] administered large amounts of L-dopa to six patients. Five showed reduction in or disappearance of muscle rigidity, got around better, and regained the sense of balance. The sixth patient showed adverse effects upon L-dopa administration but did respond favorably to 5-hydroxytryptophane, a precursor of serotonin. This favorable result was attributed to the fact that decreased muscle tone, which is sometimes present in chronic manganese poisoning but is hardly ever found in Parkinsonism, is the product of a low serotonin level in the striatum of the brain stem. Evidence that further implicates serotonin in the condition was demonstrated by Goldstein et al.[51] and Poirier et al.[52] They found that dopamine exerts its tremor producing effect by competing with serotonin for the same receptors.

6.1.6 Maximum Permissible Levels of Manganese and Prevention of Chronic Manganese Poisoning

6.1.6.1 Maximum Levels–It is generally accepted that the Threshold Limit Value of 5 mg/m^3 (8 hours per day, 40 hours per week) carries a low margin of safety for those occupationally exposed to manganese. The lowest average concentration at which a case of chronic manganese poisoning has been found is 30 mg/m^3. This occurred in a manganese mill in which the worker was exposed to manganese dioxide dust. In several steel plants in which workers were exposed to manganese fumes, even lower exposures produced chronic poisoning.[47,53]

The present Public Health Service drinking water standard for manganese is 0.05 mg/liter. Presently, there are no ambient air quality or stationary or mobile source emission standards specifically for manganese.

6.1.6.2 Elimination of Occupational Exposure–Occupational chronic manganese poisoning can be controlled if certain preventive measures are taken. These include frequent periodic examinations of all individuals who are exposed to maganese in their work. Individuals applying for work in a mine should be screened for the presence of conditions that might predispose them to manganese toxicity, such as hepatic and renal disease, blood abnormalities, organic lesions of the central nervous system, or progressive pulmonary disease. Individual proven protection measures include initial and periodic medical examinations, transfer of individuals who have liver or lung disease to areas of less exposure, and the use of hygienic measures including changing clothes after each shift to ensure cleanliness among workers.[48]

Technical measures should be directed mainly toward controlling emissions from the drilling and crushing of ores. Dry drilling of blast holes and blasting itself cause dust clouds that remain suspended in the air for long periods of time. Thus, it would be advantageous to blast at the end of the shift so that the men would be out of the mine when the manganese concentration is most intense. Ventilation should be used to remove the dust, and water spraying should be available to keep the dust down.

6.2 EFFECTS ON PLANTS

Manganese is an essential micronutrient for plants, which assimilate the element in the divalent form from the soil. Therefore, the availability of manganese to plants depends on whether it is present in soil in the divalent, tetravalent, or some other oxidation state. The form present in the soil is dependent upon the acidity of the soil, the microbial population, the presence of oxygen, and the availability and abundance of organic matter. Deficiency of manganese can often be a significant factor in reducing crop yields. Manganese deficiency commonly occurs in soils that are rich in organic matter and have pH values above 6.5.[54] It has been shown that the capacity of plants for absorbing manganese varies according to species.[24] In a study of 20 different species of flowering plants, some had a capacity for absorbing manganese that was 20 to 60 times greater than those with the lowest capacity for absorbing the element. A review by Sparr[55] indicates the fertilization requirements for different crops and soil regions in the United States.

The Mn^{2+} form of manganese, in excessive amounts, can result in manganese toxicity. Manganese toxicity usually occurs under conditions of reduced oxygen tension such as occur when soils are flooded and when the pH is on the acid side.

In one study of plant damage, celery plants in a crop grown on reclaimed deep acid peat soil developed necrotic lesions on leaflets and the petiole. Concentrations of manganese in the affected parts ranged from 10 to 270 ppm, depending on the extent to which the parts were affected.[56] In nutrient culture experiments, toxic effects developed when manganese concentrations in the tissues of tobacco reached 3,000 ppm[24] and, in mango, 800 ppm.[57] Bean (*Phaseolus vulgaris*) is particularly susceptible to manganese toxicity and has been suggested as a test organism for the study of manganese toxicity. Healthy leaves were found to contain 40 to 90 ppm of manganese and affected leaves 1,104 to 4,261 ppm.[24] Manganese tends to accumulate in the leaves of plants, thus plant tops are good indicators of the manganese concentrations in plants and in the soil.

Microbial interactions with manganese have already been discussed in the section dealing with manganese in the soil. Microbial action is extremely important in chemical transformations of manganese in the soil.

The effects of high concentrations of manganese in the soil upon plants and the microbiota have received a great deal of attention; however, the effects of high concentrations of manganese on wildlife have received little study, primarily because of lack of information.

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7. CONTROL TECHNOLOGY

7.1 INTRODUCTION

The emission of manganese particulates probably will be controlled simultaneously with particulate emissions from steel furnaces and by the same particulate control equipment. There is no assurance, however, that manganese emissions will be reduced proportionately with other particulate emissions because a high percentage of manganese emissions are fine particles less than 1 μm in diameter.

The primary deficiencies in the control of trace metals result from a lack of basic information. Before a meaningful program can be formulated and executed, key questions must be answered:

- Which of these metals are environmentally harmful?
- Where and to what extent are the harmful ones being released to the environment, and in what physical/chemical form?
- What are the best ways to control release of harmful trace metals?

All three questions are being studied by groups within EPA; the last two are being considered in various particulate emissions testing programs, in programs to develop control systems for combustion or metallurgical processes, and in clean fuels programs.

Two basic approaches are involved in EPA work currently under way on emission control technology applicable to trace metals: research and development for evaluation of existing devices for fine-particulate control and demonstration of improved particulate control systems for specific major problem industries (for example, electric utility and iron and steel). Pilot equipment for controlling sulfur oxides or particulates is also being tested to determine its capability for removing other pollutants, including trace metals such as manganese, chromium, vanadium, and nickel.

7.2 CONTROL DEVICES

Manganese from steel furnaces is controlled by various types of collectors, including electrostatic precipitators, high-efficiency wet scrubbers, and fabric filters. Four physical factors make dust collection economically difficult: the small particle size (as low as 0.01 μm), the large volume of gas, the high gas temperature, and the low economic value of the recovered material. Recent data indicate that electrostatic precipitators may be especially effective for removing fine particulates.

7.3 MANGANESE FUEL ADDITIVES

Manganese fuel additives may cause problems associated with stationary as well as mobile sources. Control of emissions from burning fuels containing antiknock and smoke-inhibiting additives may require special systems. The hazards of these organic manganese additives will be identified in EPA's fuel additive research and development program.